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Disposal of By-Products from Nonregenerable Flue Gas Desulfurization Systems
Second Progress Report

Aerospace Corp., Los Angeles, Calif.

Prepared for

Industrial Environmental Research Lab., Research Triangle Park, N.C.

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Second Progress Report

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16. ABSTRACT

The report gives results of the first 3 years of study to determine environmentally sound methods for disposing of wastes from nonregenerable flue gas desulfurization systems. Untreated and treated wastes from seven different scrubbers at eastern and western plants, using lime, limestone, or double-alkali absorbents, were characterized. Concentrations of salts and trace elements are related to potential environmental pollution for both treated and untreated wastes. Physical properties (e.g., bulk density, compression strength, permeability, and viscosity) are given. Disposal of untreated wastes in impermeable impoundments appears to be environmentally viable; however, the ability to reclaim the land has not been determined. Chemically treated sludges placed in landfills have been shown to be structurally adequate; in addition, reduction of leachate intrusion into the subsoil is achieved by the reduction of solubility, permeability, and surface water. Cost estimates for chemical treatment/disposal equate to $2 to $3 per ton of eastern coal burned; lined pond disposal costs are estimated at about 75% of chemical treatment/disposal costs. Costs for disposal of wastes--dewatered and compacted, or converted to gypsum--are being determined.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Scrubbers	Pollution Control	13B	
Waste Disposal	Sludge	Stationary Sources		
Flue Gases	Calcium Oxides	Nonregeneration	21B	07B
Coal	Limestone	Double Alkali	21D	08G
Combustion	Sorbents			11G
Desulfurization	Ponds		07A,07D	08H
Earth Fills	Leaching		13C	

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DISPOSAL OF BY-PRODUCTS FROM NONREGENERABLE FLUE GAS DESULFURIZATION SYSTEMS:

Second Progress Report

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Washington, D.C. 20460

ABSTRACT

This report provides results of the first three years (1973-1975) of a study by The Aerospace Corporation to determine environmentally sound methods for the disposal of wastes from nonregenerable flue gas desulfurization systems. Characterizations of untreated and treated wastes from seven different scrubbers at eastern and western plants, using lime, limestone, or double-alkali absorbents, have been conducted. The data presented identify concentrations of salts and trace elements related to potential environmental pollution for both treated and untreated wastes. Physical properties, e.g., bulk density, compression strength, permeability and viscosity, are given. Ponding of untreated wastes in impermeable impoundments appears to be a viable process for pollution control; however, the ability to reclaim the land has not been determined. Chemically fixed sludges in landfills have been shown to be structurally adequate. Although zero pollutant discharge of leachates from chemically fixed sludges may not be attained in all cases, the reduction of the mass release of constituents to the subsoil through the reduction of solubility, permeability, and surface water can be accomplished. Cost estimates (1976 dollars) for fixation disposal equate to $2 to $3 per ton of eastern coal burned (depending on the process selected); lined pond disposal costs of untreated materials are approximately $1.60 to $2.20 per ton of coal (depending on the type of material used); and the cost for ponding on natural clay soils is $1.00 per ton of coal.

This report was submitted in partial fulfillment of Contract Number 68-02-1010 by The Aerospace Corporation under the sponsorship of the U.S. Environmental Protection Agency. Work completed through 24 November 1975 is reported; however, selected updates have been made during the publication period.

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CONVERSION TABLE

A list of conversion factors for British units used in this report is as follows:

British	Metric
1 acre	4047 square meters
1 British thermal unit per pound	2.235 Joules per gram
1 foot	0.3048 meter
1 cubic foot	28.316 liters
1 inch	2.54 centimeters
1 gallon (U.S.)	3.785 liters
1 pound	0.454 kilogram
1 mile	1.609 kilometers
1 ton (short)	0.9072 metric tons
1 ton per square foot	9765 kilograms per square meter
1 gram per square foot	10.76 grams per square meter
1 part per million	1 milligram per liter (equivalent)
1 pound per square inch	0.0703 kilogram per square centimeter
1 cubic yard	0.7641 cubic meter

SECTION 1

INTRODUCTION

1.1 REPORT COVERAGE

This interim report presents results obtained over a three-year period of work (1973-1975) performed in a broad-based study of the characterization and disposal of the by-products from nonregenerable flue gas desulfurization (FGD) systems. This work was performed under EPA Contract No. 68-02-1010, which began on 23 November 1972 and is scheduled to continue through 23 January 1977. The first-year results have been reported in an initial report (1). This report, with some exceptions identified below, incorporates the first-year data with results obtained during the following two years and specifically covers the period of study from 23 November 1972 to 23 November 1975. Data obtained during the period of publication (after 23 November 1975) are incorporated wherever possible. A final report will summarize all data to completion as of 23 January 1977.

Exceptions to the incorporation of all results are as follows: During the second and third years of this study, the contract was modified to incorporate two new tasks so that current technological advancements could be assessed in light of the basic data produced in the general study. These tasks are as follows: (a) the Environmental Protection Agency (EPA) field disposal evaluation of treated and untreated wastes at the Tennessee Valley Authority (TVA) Shawnee Steam Plant, and (b) the assembly, assessment, and reporting of all flue gas cleaning (FGC), waste-related, research and development (R&D) activities of EPA, TVA, and private industry. These two tasks relate to specific events and, for maximum visibility into large quantities of data, are reported in separate documents: the Shawnee field evaluation project in (2), and the FGC R&D task in (3). They will also be reported in separate documents at the conclusion of the current contract period on 23 January 1977.

In addition to the reports just discussed, formal presentation of study data have been made periodically throughout the program at three EPA Flue Gas Desulfurization Symposiums (4-6), the American Society of Mechanical Engineers (ASME) Annual Technical and Environmental Symposium (7), the National Ash Association Ash Utilization Symposium (8), and two EPA Lime/Limestone Scrubbing Industry Briefings (9 and 10). Additionally, closely related data have been reported in (11).

The basic study, which is reported herein, covers the following subjects: disposal criteria, chemical and physical characterization of untreated wastes and wastes chemically treated in various laboratories, environmental effects, chemical solubility, and safe disposal methods and costs. The materials analyzed during the first three years of this study were obtained from seven different nonregenerable scrubbing systems at plants burning eastern and western coal and using lime, limestone, and dual-alkali absorbents (Table 1). Additionally, numerous samples have been analyzed from the EPA Shawnee field disposal project and reported in (2). Samples from many of these sources have been chemically fixed by three different commercial processors and analyzed in the Aerospace laboratories. (During the fourth year of this study, additional untreated samples to be analyzed will include two different types of sulfite wastes that have been oxidized to gypsum, one Shawnee scrubber waste that is ash-free, one waste produced in a carbide sludge absorbent system, and one double-alkali waste.)

1.2 OBJECTIVES AND STUDY APPROACH

The specific objectives of this study are as follows:

a. To identify environmental problems associated with FGC waste disposal by determining FGC waste chemical and physical characteristics.

b. To assess current FGC waste disposal methods, including feasibility, performance, and costs, by conducting laboratory studies of wastes under conditions associated with waste disposal; by providing engineering support and conducting chemical and physical analyses for the Shawnee field disposal evaluation; by evaluating other available data; and by conducting engineering cost studies of disposal methods.

c. To identify alternative disposal methods that provide an acceptable means of FGC waste disposal by cost-effective methods.

d. To make recommendations regarding alternative disposal approaches.

e. To assembly, integrate, assess, and report all FGC waste-related activities sponsored by EPA and industry.

The objectives of this study are to be met by (a) reviewing water quality standards and waste management regulations, and correlating this study's technical evaluations with limitations imposed by these regulations as appropriate; (b) performing chemical and physical characteristics, as appropriate, of FGC wastes, coals, makeup water, fly ash, and chemically treated wastes from EPA-specified sources; (c) surveying and

TABLE 1. FLUE GAS DESULFURIZATION SYSTEMS SAMPLED AS DATA BASE

Power Plant	Scrubber System	Scrubbing Capacity, MW (equiv)	Coal Source	Absorbent
Tennessee Valley Authority (TVA) Shawnee Steam Plant	Venturi and spray tower, prototype	10	Eastern	Lime
TVA Shawnee Steam Plant	Turbulent contact absorber, prototype	10	Eastern	Limestone
Arizona Public Service (APS) Company, Cholla Power Plant	Flooded-disk scrubber, wetted film absorber	120	Western	Limestone, fly ash
Duquesne Light Company (DLC), Phillips Power Station	Single- and dual-stage venturi	410	Eastern	Lime
General Motors (GM) Corporation, Chevrolet-Parma Power Plant	Bubble-cap tower	32	Eastern	Soda ash, lime
Southern California Edison (SCE) Mohave Generating Station	Turbulent contact absorber, pilot plant	<1	Western	Limestone
Utah Power and Light (UPL) Company, Gadsby Station	Venturi and mobile bed, pilot plant	<1	Western	Soda ash, lime

analyzing technical and economic data pertaining to FGC waste disposal; (d) planning, coordinating, evaluating, and reporting the EPA field disposal evaluation at TVA Shawnee (2); (e) continually meeting with or collecting FGC waste disposal R&D data from approximately 18 EPA-sponsored study contract teams and industry as appropriate (3); and (f) making recommendations for environmentally sound FGC waste disposal techniques. Final recommendations will be made at the conclusion of the study.

1.3 ORGANIZATION OF REPORT

Sections II and III provide conclusions and recommendations, respectively. Section IV summarizes the study findings and provides discussions and appropriate tables and figures to support the findings. Sections V through X comprise the total technical discussion.

Appendices A through E provide descriptions of scrubber systems from which samples were taken, laboratory analytical techniques, and all untreated data.

SECTION II

CONCLUSIONS AND OBSERVATIONS

These interim results are based upon current data from the ongoing Aerospace study. Updating as appropriate will be conducted in the final report in January 1977.

2.1 DISPOSAL CRITERIA

Federal criteria do not exist specifically for the disposal of flue gas desulfurization (FGD) wastes; however, EPA criteria for groundwater resulting from federal land application of waste water are the EPA "National Interim Primary Drinking Water Regulations" (12), issued in December 1975. Groundwater criteria can be met by ponding of untreated wastes in an impermeable basin or by fixation landfilling that prevents the collection of surface water. The acceptability of fixation landfilling that allows the collection of surface water generally requires a mixing of seepage with groundwater or streams if drinking water criteria are to be met.

In the absence of structural criteria, a conservative, unconfined compressive strength of 25 psi was selected in this study for sites which are to be reclaimed. Compression strength criteria can be met by (a) chemical fixation, (b) wastes converted to gypsum, or (c) wastes dewatered and mixed with fly ash and compacted.

Technical and economic studies of disposal methods as a function of waste characteristics are continuing. The results should form a significant portion of the data base from which disposal criteria can be determined.

2.2 EFFECT OF SCRUBBING PROCESS VARIABLES ON SLUDGE CHEMISTRY

Process variables affect the concentrations of soluble chemical species in system liquors through changes in process chemistry:

a. The concentration of major chemical species and trace elements in FGD waste decreases as the sludge passes from the scrubber to the disposal point.

b. The concentration of major chemical species increases with time from startup until a steady-state condition is reached for all species. Trace element concentrations reach steady state rapidly and are not affected by major species steady-state conditions.

e. The scrubber pH is responsible for trace elements leaching from fly ash; the pH of the system downstream of the scrubber does not affect the concentration of these trace elements in the scrubber liquor.

2.3 TRACE ELEMENT CONTENT

The trace element content in FGD sludge is a direct function of the combustion products of coal:

a. A direct correlation exists between the trace element content of coal and the trace element content in FGD wastes.

b. Fly ash represents the major source of trace elements in all but the most volatile elemental species (e.g., mercury and selenium) that are scrubbed from flue gases.

2.4 PHYSICAL PROPERTIES

The behavior of FGD wastes in a disposal site is a function of the unique physical properties of the wastes:

a. The permeability coefficients of untreated FGD wastes are typically 10^{-4} cm/sec and of treated wastes are 10^{-5} cm/sec or less [based upon sample materials fixed by Chemfix, Dravo, and IU Conversion Systems (IUCS)].

b. Pumpability (<20 poises) was found for untreated wastes having a solids content that ranged between 32 and 70 percent.

c. Bulk densities of untreated wastes as a function of dewatering techniques and material characteristics varied between 1.30 and 1.87 g/cc.

d. Compaction of untreated sludges dewatered to about 80 percent solids produced permanent displacement of 1 to 4 percent.

e. Treated wastes have unconfined compression strength greater than 1.8 tons per square foot (25 psi).

2.5 CHEMICAL PROPERTIES

The soluble chemical content of FGD waste liquors typically have approximately 10,000 mg/l total dissolved solids (TDS)(steady state), except for double-alkali scrubber systems, whose liquors have a much higher TDS. Trace elements lie typically between 0.01 and 1 mg/ℓ depending on coal content and fly ash collection techniques:

a. The leachate quality of rainwater percolated through untreated FGD waste attains a nearly-constant, TDS content of 2000 mg/ℓ, primarily sulfate salts, after passage of 5 pore volume displacements (PVD). Initial leachate content is as high as the soluble chemical content and is dependent upon the type of FGD system. Leachate through treated FGD waste has initial dissolved solids content of nominally one-half that of untreated waste and after 5 PVD attains a level of one-half to one-fourth that of the leachate from untreated wastes.

b. Mass loading to subsoil having a permeability coefficient of 10^{-5} cm/sec from FGD disposal sites by rainwater leaching varies from a high value of ~1 g/cm^2/yr for ponding of untreated waste that is continually covered with water to a low value of 0.01 g/cm^2/yr for dry disposal of treated waste. Chemical treatment makes possible a disposal method that minimizes seepage and solubility, thereby producing pollution loadings that are 20 to 40 times less than that of the disposal method for untreated sludge in which a liner is used and supernate is recirculated to the scrubber.

2.6 DISPOSAL COST ESTIMATES

Total disposal cost estimates based upon 30-year averages are as follows:

	$/Ton Sludge (Dry Basis)	$/Ton Eastern Coal Burned	Mills/kWh
Ponding with Natural Clay Base	3.50	1.00	0.43
Ponding plus Liner	5.70 - 7.80	1.60 - 2.20	0.7 - 1.0
Chemical Fixation	7.30 - 11.40	2.10 - 3.20	0.9 - 1.4

Ranges for each category shown result from variations in types of sludges and methods available for disposal. (Limiting conditions for these costs are given in Section IV, Table 7.1) Costs are in January 1976 dollars.

SECTION III

RECOMMENDATIONS

In this study, two current areas of study have been identified in which a more complete understanding and more accurate definition of environmentally sound disposal methods can be attained through a greater emphasis of effort. These are (a) the correlation of disposal data with disposal criteria, and (b) field evaluations of operational-type, commercial disposal systems. EPA projects in both of these areas are in progress, but experience gained in the Aerospace study indicates that a broader scope of effort now is advisable and can produce the necessary data in a reasonably short time period. Recommendations are as follows.

3.1 DISPOSAL CRITERIA

Because no federal criteria exist for the disposal of flue gas desulfurization (FGD) sludges and because of the wide variations in sludge characteristics, disposal methods, and site characteristics, a data base is being developed by EPA from which disposal standards can be developed. Additionally, the neutralization of effluents from a disposal site by soil attenuation and mixing with groundwater and streams before the water reaches the consumer tap or other points of uptake indicate that a high degree of conservation may not be necessary in the control of sludge disposal in most localities. This is highligited by the usually low concentrations of trace elements in seepage liquors, although higher than allowed in drinking water, and the fact that the contained salts of interest, chlorides and sulfates, are not toxic compounds. Assuming that the site is managed so that a direct discharge, seepage, or runoff is not directly consumed, it may be possible to demonstrate that any of the following is possible:

a. Regulate control of treated or untreated sludge by definition only of the disposal conditions, procedures, and site arrangement.

b. Allow untreated sludges, limited by site conditions.

c. Allow treated or conditioned sludge leachate constituent concentrations in excess of drinking water criteria, but less than in an untreated liquor for all sites or as limited by site conditions.

d. Allow defined treated or conditioned sludge constituent mass release for all sites or as limited by site conditions.

It is recommended, therefore, that detailed disposal case studies be conducted for selected representative sites, with consideration given to the type of sludge that may be produced at each site; the site-specific conditions, e.g., climatological, hydrological, and geological; and the disposal method or methods appropriate for each site. Data produced in the ongoing 19 EPA FGC disposal projects (3) including material characterizations, soils studies, alternative disposal methods studies, and criteria data base development studies should be used to determine the environmental acceptability of these disposal conditions for human, animal, marine, and agricultural consumption, as appropriate. These analyses with few, if any, exceptions should provide a major and possibly conclusive answer to the criteria necessary for FGC disposal.

3.4 FIELD EVALUATIONS

The EPA is currently conducting two field disposal evaluation projects using treated and untreated sludges, i.e., the TVA-Aerospace Shawnee project, which has been in operation for approximately 18 months, and a planned Louisville Gas and Electric project scheduled to begin in the summer of 1976. A valuable assessment tool can be made available through minor modifications at the Shawnee site. That project includes the study of potential environmental impact conditions of three different commercially treated sludges disposed under worst-case conditions in which rainwater is trapped on the surface in such a way that seepage is maximized. Those studies have already shown that the seepage from treated sludges contain constituent concentrations, though considerably less in quantity than in untreated sludge seepage, are initially in excess of drinking water criteria. It is also known that no seepage will occur if no hydraulic head exists.

It is therefore recommended that after monitoring has been conducted for approximately two years, at which time a reasonable understanding of those materials will have been attained, at least two of the three treated disposal ponds should be modified to prevent the occurrence of standing water. The primary purpose will be to determine whether seepage is prevented, by monitoring the existing leachate wells, and if it is not totally prevented, then, the degree of reduction can be assessed. A secondary benefit will be the determination of suspended solids in the runoff. Dissolved solids in the runoff from such sites are not expected to be a major problem, but this factor would be determined in simple laboratory tests because the age of these ponds precludes a meaningful measurement of dissolved solids.

This modification to the Shawnee project will provide valuable data regarding the benefit of proper site management.

SECTION IV

SUMMARY

A summary highlighting results of the total effort to date is presented in this section. Brief discussions of each area of investigation are given, and selected figures and tables are included to either simplify the summary or to provide the data necessary to complete the discussions. Figures and tables are repeated as appropriate in the following sections when necessary to complete the detailed technical descriptions therein.

4.1 DISPOSAL CRITERIA

The concern in this study regarding disposal criteria is (a) for the quality of groundwater or surface waters after the introduction of flue gas desulfurization (FGD) waste liquors by means of seepage or runoff, and (b) for the structural quality of the waste materials if the disposal site is to be reclaimed. General conditions of wastes being studied for disposal in ponds or landfills include untreated wastes, dewatered and compacted wastes, gypsum, and wastes fixed by chemical processing. Systems that have a supernate or underdrainage operate in a closed loop, thereby preventing a direct discharge problem. The environmental effects to be considered, then, are leachate migration to groundwater in all cases, runoff from fixed wastes in landfills, and strength of all fixed and all conditioned (e.g., dewatered) wastes. One exception is a fixed material placed upstream of a dam from which surface water (supernate and rainfall) is occasionally discharged to a stream.

No federal criteria apply specifically to these disposal conditions; however, at this time, the EPA is conducting a study to establish a data base for the development of standards for the disposal of flue gas cleaning (FGC) wastes (3). Eventually, federal or state regulations will apply as a result of the "Resource Conservation and Recovery Act of 1976," Public Law 94-580, 21 October 1976 (13). Because of the wide variations in the characteristics of wastes, weather, soils, topography, and groundwater from site to site, permits are currently being written and applied on a site-specific basis. At this time, it appears that local regulations attempt to attain a zero pollution discharge and that all FGC wastes must be either fixed or impounded in an impermeable basin. The federal regulation that most nearly relates to a limit on seepage water quality is the EPA "Alternative Waste Management Techniques for Best Practicable Waste Treatment," issued in the *Federal Register* (14). However, these criteria apply to public-owned treatment and land application of waste water and not to disposal of FGC wastes.

These federal criteria define that the groundwater, resulting from land applications of waste water, shall be limited to the maximum contaminant levels contained in the "National Interim Primary Drinking Water Regulations" (NIPDWR) (12) or to the existing concentration, whichever is greater, "if the groundwater criteria should be established by the Regional Administrator . . . ." The NIPDWRs apply, however, to the concentrations at the consumer tap and are similar to the United States Public Health Service (USPHS) 1962 standards (15), but in contrast to USPHS no limits are given in the NIPDWR for sulfate or chloride. Because the concentration of constituents within any leachate seepage that may occur from untreated and treated wastes (during the filling period and early stages of seepage, thereafter) exceeds drinking water criteria (Table 4) it appears that some form of attenuation or prevention is needed. Possible approaches, either individually or in combination, are as follows:

a. Eliminate seepage by using lined basins.

b. Reduce seepage by using lined basins.

c. Attenuate constituents via cation exchange and adsorption in the soil.

d. Provide a means of mixing seepage with the groundwater.

e. Provide a means of mixing seepage and groundwater with connecting streams.

f. Chemically reduce solubility and permeability and provide a means of mixing seepage with groundwater.

g. Chemically reduce solubility and permeability and reduce or eliminate seepage via runoff of rainwater.

Additionally, certain structural qualities must be attained if the site is to be reclaimed. In the absence of specific criteria, a selection in this study of 25-psi minimum unconfined compressive strength has been made.

Currently, studies are continuing in this program, other EPA projects, and in industry to define and evaluate environmentally sound, least-cost methods of waste disposal, covering the range of (a) ponding; (b) dewatering, mixing with fly ash and compacting; (c) conversion to high solids content gypsum; and (d) fixation. Data from these studies are expected to provide a data base from which an appropriate disposal mode can be selected for any given site.

4.3 PHYSICAL PROPERTIES

The physical properties measured in this study for the characterization of FGD sludges include the wet bulk densities of the sludges as a function of dewatering processes, the coefficient of permeability, the viscosity as a function of water content, the compactibility, and the unconfined compressive strength as a function of moisture content. Further characterization includes the identification of the crystalline phases in each sludge, the relative quantity of each phase, and the morphological description of each phase. In addition, sludge samples chemically treated by commercial processors are evaluated with respect to their coefficient of permeability and unconfined compressive strength. An interpretation of the resultant behavior of all experimental tests performed is made relative to the physical or chemical characteristics of each sludge, and an evaluation is made of these behavioral effects on the requirements for environmentally safe disposal.

4.2.1 Wet Bulk Density

The dewatering characteristics of FGD sludges are important to the various disposal techniques in that they affect the volume of the disposal basin, the methods of handling the sludges, and the condition of the sludges in their state of ultimate disposal. All of these variables affect the economics of disposal as well as the pollution potential of the resultant waste. The ability of a sludge to be dewatered is primarily a function of the size and distribution of particles and the morphology of the particles determined by crystalline phase. In this study, four methods of dewatering were investigated in the laboratory: settling, settling by free drainage, vacuum filtration, and centrifugation. These methods are those most often used or considered because of their relative cost effectiveness.

The results of this study reveal that all dewatering behavior responds to a relationship that relates the wet bulk density ρ_B of a material to the weight fraction f_s, the true density ρ_s of the solid phase, and the density of water ρw, by the equation:

$$\rho_B = \frac{\rho_s \, \rho_w}{\rho w \, f_s + \rho_s (1 - f_s)} \qquad (1)$$

This relationship corresponds to a condition in which the water content of the dewatered sludge exceeds the amount just necessary to fill the void spaces when the particles are closely packed together. The dewatering method and the characteristics of each sludge establish particle packing that can be determined by measuring the dry bulk density of the sludge when all water has been dried from the sample. If water is incrementally added to the dried sample, the wet bulk density will increase relative to the dry bulk density ρ_D, by the equation:

$$\rho_B = \frac{\rho_D}{f_s} \qquad (2)$$

When sufficient water is added to just fill all void spaces between particles, ρ, the maximum density for that sludge, is reached and is defined as the coincidence of the two equations.

If the dewatering efficiency of each method is defined as the percent of the measured wet bulk density relative to the maximum density attainable, a means of comparing the efficiency of each method is available. In all cases, the highest dewatering efficiency was obtained by vacuum filtration (93.6 average percent), and the lowest efficiency was by centrifugation (81.9 average percent); settling (86.2 average percent) and free drainage (87.2 average percent) efficiencies lie in between. However, when actual wet bulk densities are compared as in Table 2, it is seen that there is little difference between vacuum filtration and centrifugation and, in some cases, centrifugation produces the most dense sludge among the four methods being evaluated.

The discrepancy is explained by the difference in particle packing that results from each method. Centrifugation is a high-force method that packs particles closely together, but when performed in a glass vial water is not efficiently removed from between the particles. Vacuum filtration is a method that uses considerably less force and may result in poor particle packing relative to the applied force. The vacuum-assist is most effective in removing the water from between the particles, and this is the primary source of the high dewatering efficiency. Settling with or without drainage is a low-force method, and particle packing is generally poorest. The difference between these two methods is a consequence of the loss of some water by drainage.

When industrial filters and centrifuges are used rather than laboratory equipment, filtration is generally slightly less effective with a resultant decrease in dewatering efficiency. On the other hand, centrifugation is usually less effective in particle packing and more effective in removing water because of a difference in mechanism for separating water from solids. Thus, in field conditions, the efficiency of dewatering by these two methods is more nearly equivalent, with a general tendency for centrifugation to provide more consistent results. Settling methods are always less effective than either filtration or centrifugation, but in many cases their use constitutes the most cost-effective dewatering method.

4.2.2 Coefficient of Permeability

The physical parameter that most significantly affects the pollution potential of a sludge is the permeability of the sludge to rainwater since this parameter governs the amount of leaching water passing through the sludge. Disposal techniques are developed that can minimize the recharge of rainwater to subsoils, but in all cases the permeability coefficient defines the maximum limit to the amount of liquid that can pass through the sludge.

The coefficient of permeability was measured on both untreated sludges and sludge chemically treated by several processors. Permeation columns were constructed by generally accepted methods (Section 6.5.1), and

TABLE 2. WET BULK DENSITIES OF FGD WASTE AS A FUNCTION OF DEWATERING METHOD

Sample Source and Date	Dewatering Method							
	Settled		Settled and Drained		Centrifuge		Filter	
	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc	Percent Solids	Density, g/cc
Shawnee Limestone, [illegible]	47.0	1.45	55.7	1.50	59.6	1.56	65.0	1.65
Shawnee Limestone, [illegible]	52.7	1.46	56.3	1.53	63.1	1.60	65.9	1.66
Shawnee Lime, [illegible]	40.7	1.34	43.4	1.39	49.9	1.48	56.0	1.51
[illegible]	38.0	1.35	45.9	1.39	58.9	1.45	57.8	1.52
[illegible]	37.2	1.30	43.4	1.37	62.2	1.62	58.6	1.58
[illegible] Lime, [illegible]	47.6	1.40	51.3	1.46	57.2	1.52	57.0	1.52
Cholla Limestone, [illegible]	36.7	1.29	50.9	1.46	60.9	1.56	71.4	1.48
[illegible] Limestone, [illegible]	44.6	1.45	47.2	1.47	77.0	1.86	80.3	1.74

the rate of water passage through the columns was measured with time and as a function of hydraulic head. In some cases, packed sludge columns were compacted to greater particle packing densities, and the measurements were then repeated. The measured permeability coefficients are plotted as a function of void volume in Figure 1.

The results of these measurements show that the permeability coefficients of all the untreated sludges are approximately 1×10^{-4} cm/sec, and generally between 2×10^{-4} and 5×10^{-5} cm/sec, as shown in the shading in Figure 1. These results also show that for any specific sludge, the expected relationship of decreasing permeability with decreasing void volume appeared. A correlation with particle size as well as particle packing fraction explained the permeability behavior of FGD sludges, but exceptions to the general observation prevent establishing a direct correlation.

Chemically treated sludges are plotted in Figure 1 as specific datum points, and it is seen that the permeability of these materials is nearly identical to the permeability of untreated sludge. It must be noted, however, that all of these measurements were conducted on treated sludges that were pulverized in order to pack the permeation column. In this condition, the columns represented material that has been placed and cured, and subsequently moved and replaced. Although this method of disposal is intrinsically expensive, it is and has been practiced at several power plants and represents a state-of-the-art technique.

Alternatively, some treated sludges were measured in a solid condition that precluded fracturing at any time. The values of permeability measurements were as large as 10^{-7} to 10^{-8} cm/sec. However, permeability measurements of sludges treated under field conditions (2) have shown that the permeabilities of the treated sludges range from 10^{-5} to 10^{-7} cm/sec.

4.2.3 Viscosity

The viscosity of FGD waste slurries is a direct measure of its pumpability. Thus it affects handling procedures, transporting, and waste disposal methods. Moreover, basic system design considerations are affected by the relative ease of pumping the waste to desired locations. FGD wastes contain finely divided particulate matter suspended in a water system. This particulate matter tends to range from colloidal size to about 100 μm and consists of three major phases having markedly different morphologies. It is both the particle size distributions and phase morphologies that are believed to influence the viscosity of the sludges. Measurement procedures are described in Section 6.2.2.1.

Viscosity measurements were performed on sludges at varying water contents in ambient temperatures with a commercial viscometer having a measuring range from 3 to 150 poise. Measurement procedures are

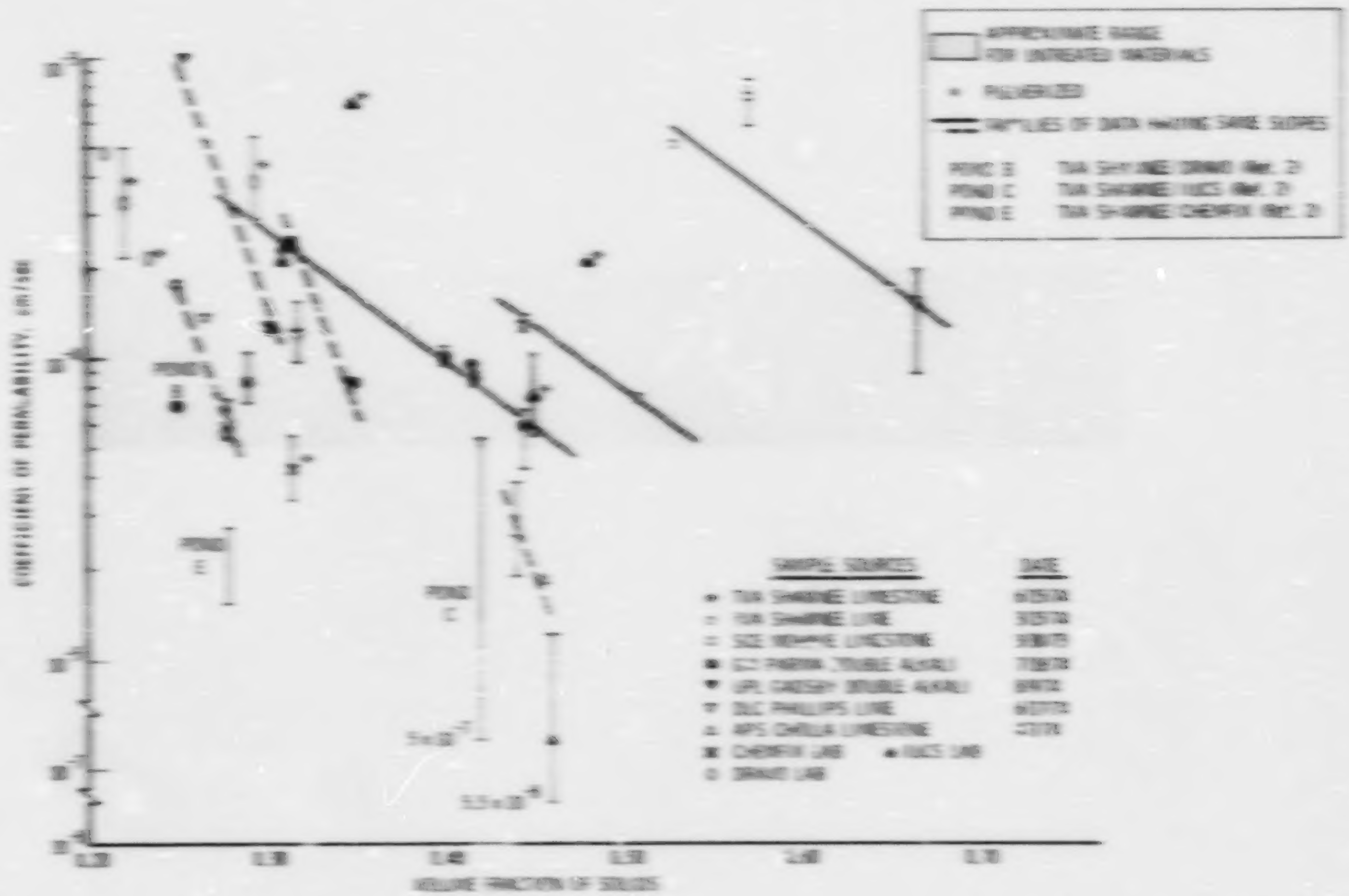

Figure 1. Permeability of treated and untreated sludge: Aerospace analyses.

described in Section 6.3.1. The results of the viscosity tests are presented in Figure 2 for the seven sludges measured and reveal that easily pumpable mixtures (< 20 poise) range from a high solids content of 70 percent to a low solids content of 32 percent. In addition to the position of each viscosity curve on the graph, these results further reveal that the slope of the viscosity curves can be separated into two groups.

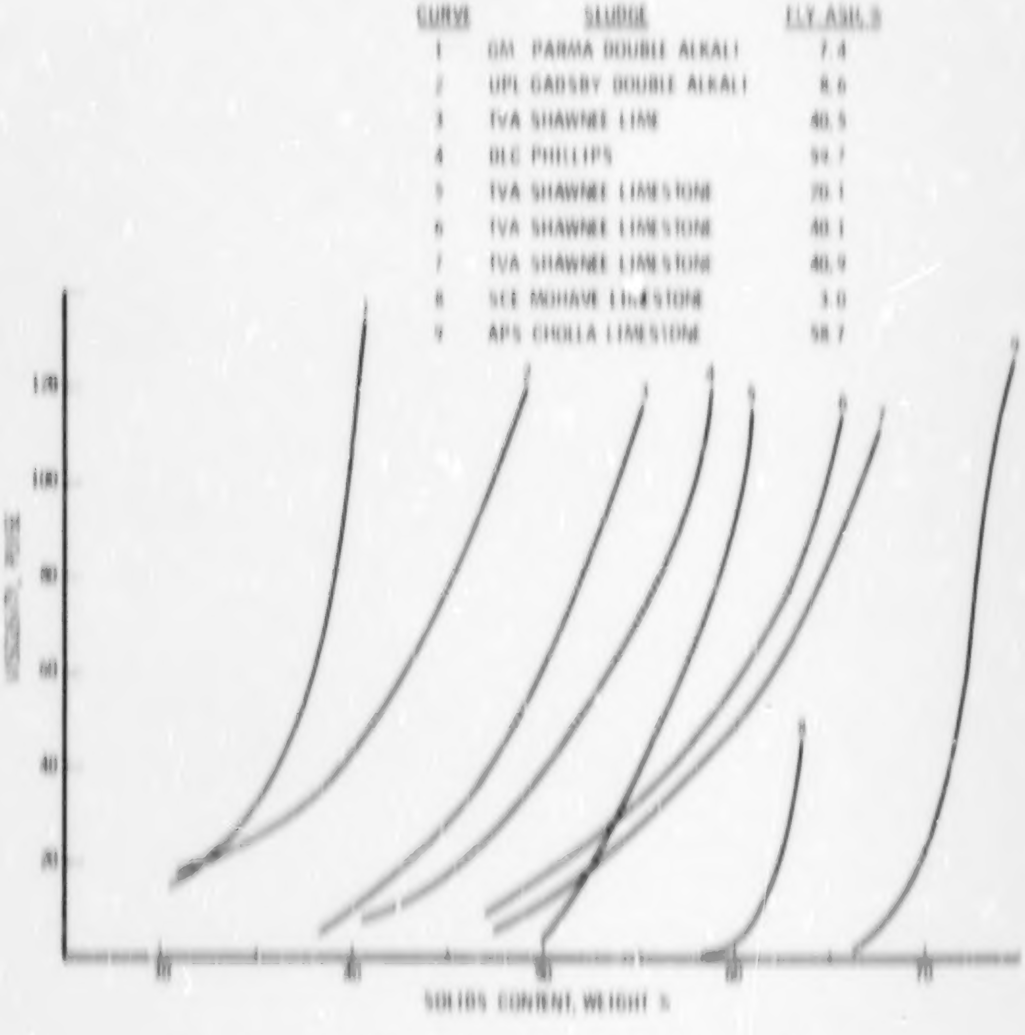

Figure 2. Viscosity of desulfurization sludge.

Whereas particle shapes, particularly the platey sulfite particles have been credited with the change in the rheological nature of sludge, in the viscous-fluid behavior of these sludges it is not apparent that the sulfite phase plays a decisive role. On the other hand, these data clearly suggest that fly ash increases the fluidity of a sludge and high pH may increase its viscosity. Whereas particle shape, size, and distribution appear to influence viscosity behavior, the precise effect each may have is not clear from these limited data.

4.2.4 Compaction

The compaction capability of FGD sludges can be an economic asset by providing a means of increasing the mass of waste disposed of within a specified volume. Moreover, if compacted sludge behaves like fly ash, significantly reduced permeabilities and increased strength can be expected, and these may increase the environmental acceptability of the sludge. The compactability of a sludge is dependent upon particles rearranging under an applied force by sliding past each other. This process is enhanced by the presence of some pore water, which acts as a lubricant, but there must also exist air voids into which the particles can move. The particle size distribution and crystalline morphology are the two most important parameters influencing the compactability of FGD sludges.

The same nonvibratory compaction test was performed on each of six FGD sludges at nominally 100 psi. Dried sludge samples were loaded into pellet dies for the tests, and the change in sample heights were noted. While constrained by the die, the samples deflected as much as 15 percent under the load; however, when removed from the die, the actual compaction ranged between 1 and 4 percent as shown in Figure 3. In contrast, related studies on fly ash have been shown to compact from 7 to 20 percent (16).

The lack of compaction for FGD sludges was explained by the crystal structure of the calcium sulfite platelets and the interwoven lath-like structure of the calcium sulfate crystals. In many cases, the presence of water in the pores increased the deflection under load but contributed little or none to the permanent deformation. The absence of significant permanent deformation resulted in no measurable increase in strength and in a limited decrease in permeability to water percolation. These tests suggest that, while some benefit may be gained by compaction, it is not likely to be a cost-effective operation in untreated sludge disposal.

4.2.5 Compressive Strength

Strength measured in an unconfined condition was compared with unconfined strength data of soils. These tests provide a means of evaluating the suitability of FGD wastes in landfill and structural fill situations.

Unconfined compression tests were conducted by standard test methods for treated and untreated FGD wastes. The results of these tests are summarized in Table 3 for samples tested in a dry condition (no free

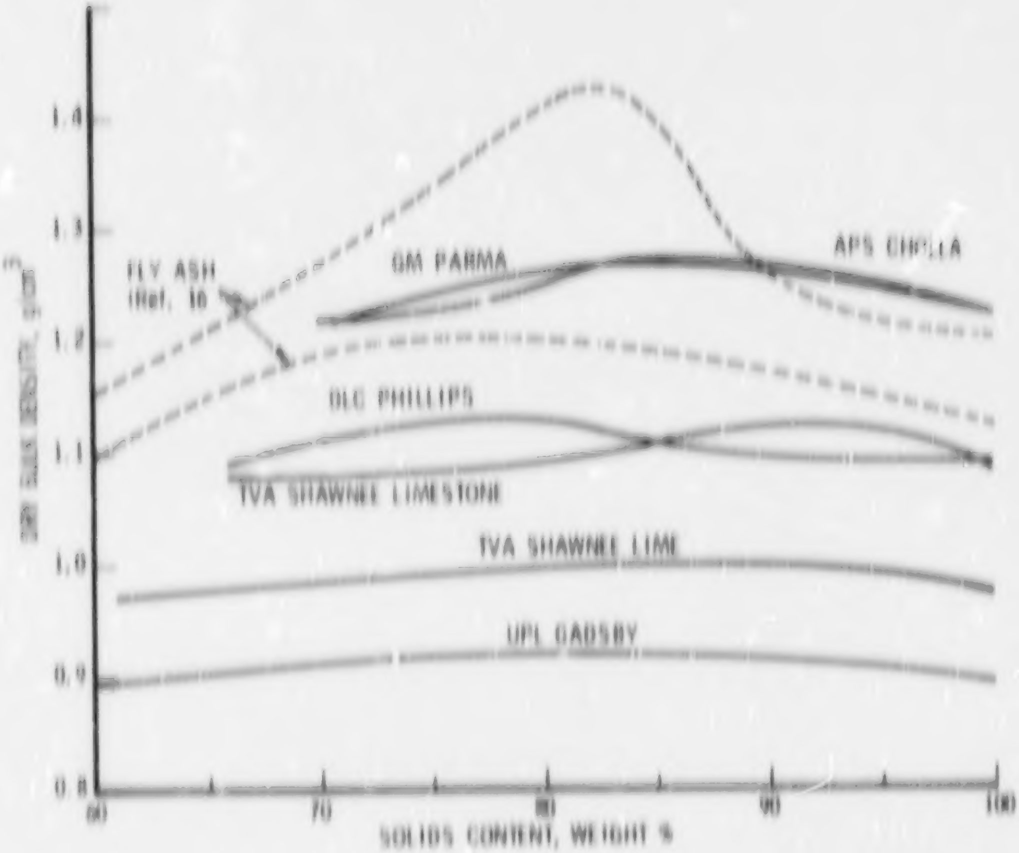

Figure 3. Compaction of FGD sludge (dry basis).

water), a damp condition (partial pore water), and wet (as placed operationally). The results indicate that, on an overall basis, untreated FGD wastes in a damp condition (~8% water) are stronger than samples that are dried of all water. Nevertheless, these data indicate that untreated sludges, having a solids content of approximately 85 percent or greater, have unconfined compressive strengths similar to those of natural soils.

Treated FGD wastes have strengths that are capable of structural landfill applications. The data do not show an appreciable difference between the strengths in the dry or wet conditions.

4.3 CHEMICAL CHARACTERIZATION

Chemical analyses from all sampling points from lime, limestone, and double alkali scrubber waste streams are summarized in Table 4, where the range of concentrations for each chemical species is given. The

TABLE 3. UNCONFINED COMPRESSIVE STRENGTH TEST RESULTS SUMMARY

FGD Waste	Range of Water Content, %	Strength Range, Ton/ft^2
Untreated	5.6 - 14.4 0.0 >10[a]	0.9 - 2.4 0.6 - 1.5 0.0
Treated	2.4 - 5.6 0.0 (35 - 60)[a]	25.4 - 48.5 22.3 - 52.3 1.8 - 39

[a] Typical conditions in place.

distribution of trace elements in system liquors tends to lie between 0.01 and 1 mg/ℓ for all elements except mercury, which has a concentration distribution about one-tenth that of other trace elements. In the solids portion, the trace element distribution is approximately two orders of magnitude greater than the liquor.

Major chemical species concentrations in liquors depend strongly on the scrubber system parameters and tend to have total dissolved solids content of about 10,000 mg/ℓ except during startup and in selected exceptions. The chloride concentration in the liquor depends primarily on the chloride content of the coal. Major chemical species content in the solids also depends upon system parameters, primarily oxidation conditions and fly ash collection methods.

The crystalline phases present in the solids portion of each FGD waste are presented in Table 5. These data reveal that gypsum and calcium sulfite hemihydrate are the principal sulfur products and that a broad range of fly ash contents (3 to 60 percent in this study) might be expected from a survey which includes both eastern and western coal, with either separate or simultaneous fly ash collection. Several soluble phases were present as a consequence of salt formation during drying of occluded water. The presence of limestone in all samples is a consequence of both unreacted limestone absorbent and carbonate formation by adsorption of carbon dioxide from the atmosphere.

The chemical pollutants in FGD sludges originate from process ingredients, coal, combustion products, absorbents, and process makeup water. The chemical characterization of FGD sludges included analytical measurements of both the solid and liquid fractions of sludge sampled at various positions along the scrubber circuits. Process ingredients from which the chemical pollutants originate were also analyzed in order to provide

TABLE 4. CHEMICAL CONSTITUENTS IN LEACHATE FROM UNTREATED AND CHEMICALLY TREATED FGD WASTE AFTER 1 AND 50 PVD (CONCENTRATIONS IN mg/ℓ)

Chemical Constituent	Untreated Waste		Treated Waste	
	1st PVD	50th PVD	1st PVD	50th PVD
Arsenic	0,02	0,004	0,015	<0,004
Beryllium	0,01	<0,004	0,008	<0,002
Cadmium	0,015	0,002	0,02	0,002
Chromium	0,045	<0,003	0,06	0,003
Calcium	0,045	0,010	0,025	0,005
Lead	0,25	0,010	0,15	0,03
Mercury	0,0005	<0,00005	0,0007	0,0002
Selenium	0,055	0,006	0,040	0,008
Zinc	0,65	0,04	0,27	0,03
Chloride	2600	100	600	75
Fluoride	4,0	0,8	1,1	0,4
Sulfite	50	30	15	20
Sulfate	6500	1200	3500	450
Total Dissolved Solids	10,000	2200	6000	1000
Chemical Oxygen Demand	10	6	7	4
pH	6,6	5,5	6,8	8,0

TABLE 5. PHASE COMPOSITION OF FGD WASTE SOLIDS IN WEIGHT PERCENT

Phase Formula	TVA Shawnee Limestone, [illegible]	TVA Shawnee Limestone, [illegible]	TVA Shawnee Limestone, [illegible]	TVA Shawnee Lime, [illegible]	SCE Mohave Limestone, [illegible]	GM Parma Double Alkali, [illegible]	APS Cholla Limestone, [illegible]	DLC Phillips Lime, [illegible]	[illegible] Double Alkali, [illegible]
$CaSO_3 \cdot \frac{1}{2}H_2O$	21.4	15.6	31.2	6.3	86.4	48.2	17.3	29.8	61.8
$CaSO_4 \cdot 2H_2O$	18.9	21.6	21.4	46.8	6.2	12.9	18.6	12.9	0.7
$CaSO_4 \cdot \frac{1}{2}H_2O$						19.2			
$CaCO_3$	14.7	20.2	4.[illegible]	2.5	[illegible]	7.7	2.5	3.2	18.8
$MgSO_4 \cdot 7H_2O$	4.6	1.7	1.9	1.9					
$Na_2SO_4 \cdot 7H_2O$						6.9			
NaCl					2.9				
$CaSO_3$*									17.7
Fly Ash	25.3	40.[illegible]	40.3	42.5	1.3	7.4	58.7	53.7	6.6
Total	101.8	101.[illegible]	99.5	100.2	102.4	101.4	96.[illegible]	[illegible]	100.[illegible]

*Phase not explicitly measured; presence deduced from x-ray data.

an understanding of the relationship between the source and fate of these potential pollutants within the FGD scrubbing processes.

4.3.1 Generation of Trace Elements in FGD Wastes

Chemical analyses of FGD sludges identified trace elements in both the solid and liquid fractions of the sludges (Table 4). When the specific analyses are plotted against the analyses for coal (corrected for other process ingredients), a relationship is shown, as in Figure 4 for solids and Figure 5 for liquids (see Section VII, Figures 27 and 28 for details). This relationship shows the direct relationship between the trace elements in sludge and those in coal. In general, these data indicate that approximately one percent of the trace elements in the sludge is distributed in the liquid fraction.

The correlation that exists between the trace element content in coal and the trace element content in fly ash further suggests that fly ash is the principal source of these trace elements in the sludge. Whereas the data base in this study is not adequate to unequivocally explain fully the source of trace element content in the sludge, the contribution due to fly ash as described in the literature sources must be recognized.

Since the direct relationship between trace elements in sludge and in coal is clearly indicated, the trace metals from western coal, having typically lower concentrations of arsenic, cadmium, mercury, and zinc than eastern coal are expected to produce sludges having lower concentrations of these elements. This behavior was found as expected.

4.3.2 Process Variables

The chemistry of the scrubbing liquor is affected by the absorbent used in each system. It is found that, in general, the trace element content in the liquor is highest in the limestone systems, intermediate in the lime systems, and lowest in the double-alkali systems. The only readily recognized systematic parameter that can affect these differences is the pH within the scrubber. Among them, the limestone scrubber operates at the lowest pH and the double-alkali system at the highest pH. When specific systems are compared on a one-to-one basis, the apparent relationship between scrubber pH and trace element content is confirmed in every case. This effect is interpreted as a consequence of trace elements leaching from fly ash during the most acid part of the recycle system.

An evaluation was made of the trace element content in the system liquor at various positions in the scrubber process. Chemical analysis indicated that the system liquor pH increased and trace element content showed a slight decrease enroute from the scrubber to the disposal site. The results for trace elements may be interpreted as a response to system pH or a response to the changes taking place in the concentration of major chemical species. The in-process analyses showed, for the major species, that a rapid oxidation of sulfite ion and the precipitation of calcium sulfate also take place enroute to the disposal site. The trace element content in the liquor may

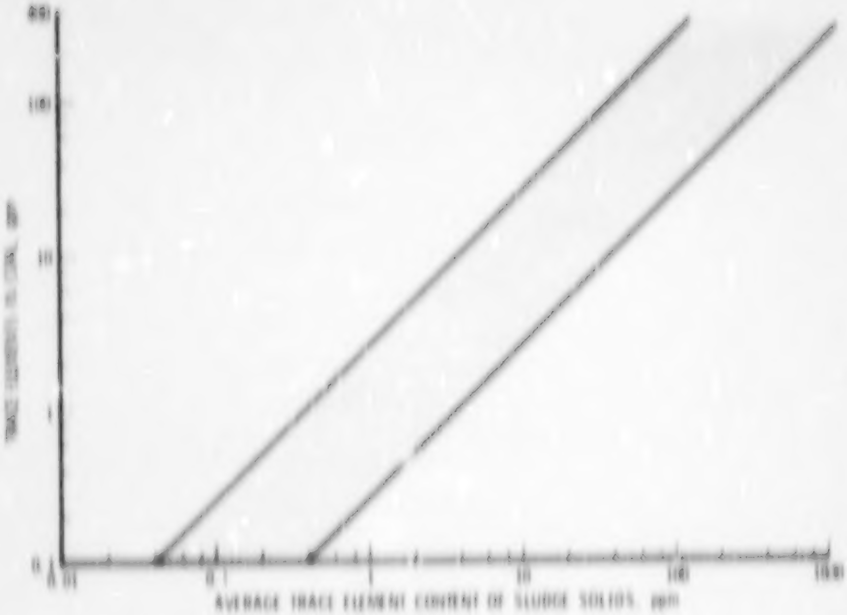

Figure 4. Relationship between trace element content in coal and sludge solids.

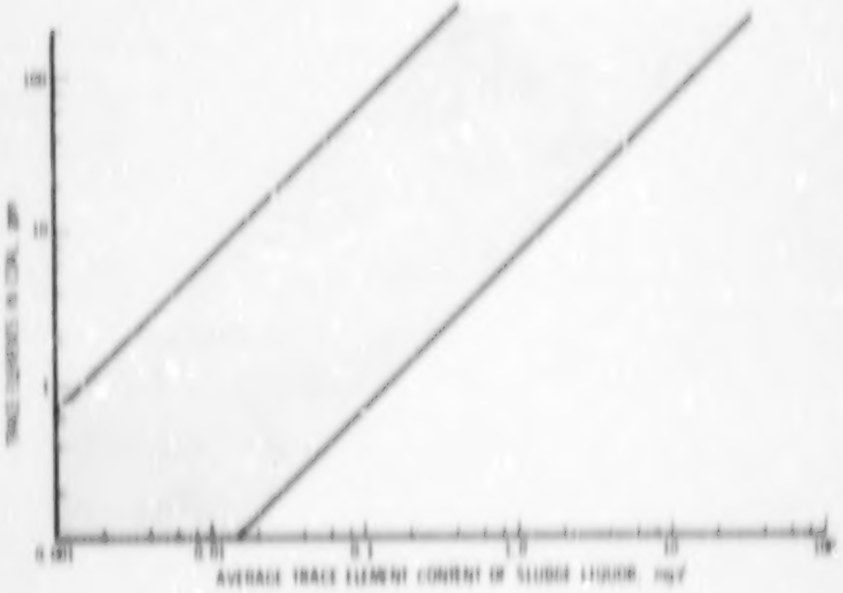

Figure 5. Relationship between trace element content in coal and sludge liquors.

be decreasing by precipitation in response to decreasing ionic strength, by coprecipitation resulting from the scavenging action of the calcium sulfate, by adsorption onto newly created crystal surfaces of the calcium sulfate phase, or by the pH changes previously discussed.

An evaluation of all chemical analyses of trace elements in the liquor was made as a function of both pH and ionic strength. No correlation was found for any element when chemical data from all systems were simultaneously compared, and it must be concluded that neither pH nor ionic strength are primary variables. However, when chemical data were compared within a single system, a pH correlation was found. Thus, it is concluded that the primary source of trace elements is the coal, and these elements enter the scrubber system primarily by leaching from fly ash in the scrubber. The pH of the scrubber affects the trace element content in the liquor, but the pH of the system downstream of the scrubber is shown to have only a minor effect on this value.

When the chemical species in system liquor are evaluated over a period of time, the data indicate that all species increased from startup. The calcium sulfate saturation level is established quickly as is the concentration of trace elements. Chloride ion concentrations appear to build up at a slower rate and continue to build up until a steady state is established. As the chloride ion concentration increases, it effects an attendant increase in ionic strength that increases the calcium sulfate equilibrium levels. Trace element contents do not reflect these changes either from a lack of analytical sensitivity at very low concentration, from a lack of accuracy of analytical data, or from a lack of response to changes in major species concentrations.

4.3.3 Chemical Solubility Analysis

A comparison of experimental scrubber liquor compositions with compositions calculated from the assumption of equilibrium solubility was made for each analysis presented in Appendix D by using two different computer programs. One program was specifically designed to predict maximum concentrations of trace chemical species as a function of the concentration of major species from empirical solubility data. The other program was designed to predict major species concentrations in a liquor from thermodynamic data, but the trace chemical species concentrations were not predicted.

When the results of the two programs are compared for major species, it is shown that the two programs are in virtual agreement with respect to the saturation of calcium sulfate in every analysis and saturation of calcium sulfite in only a few cases. Moreover, the agreement between the two independent approaches relative to the experimental data provides supportive evidence to the accuracy of the experimental measurements.

For the nine trace elements measured, there was no evidence that trace element saturation was the controlling parameter for the trace metal concentration in the liquor. This finding is consistent with the finding of an absence of trace element response to changes in major chemical species within the liquor system. For several trace elements, anomalies exist relative to the measured versus expected concentrations and require further experimentation to resolve.

4.4 ENVIRONMENTAL ACCEPTANCE OF FGD WASTE

An evaluation of the environmental impact of FGD waste was made as a consequence of the alternative routes of pollution to the environment and the methods by which the wastes may be disposed of. The accessibility of pollutants to the environment can be minimized by (a) decreasing the permeability of the wastes to reduce the seepage of water, (b) reducing the leachability of the wastes through a reduction of the solubility of the material, and (c) managing seepage and runoff to limit the excess of waste constituents to groundwater or surface waters. Disposal concepts include (a) chemical treatment of waste to affect alternation of its permeability and leachability properties, (b) total impoundment of untreated or treated wastes to isolate them from the environment, and (c) several methods of impounding untreated but dewatered wastes. Many of these concepts produce a structurally soluble material which makes site reclamation possible. The assessment of these methods shows that although intrinsic pollution potential of each method is different from the other, the protection of the environment is best assured only through the implementation of appropriate disposal site management techniques.

4.4.1 Pollutant Access to the Environment

An evaluation of the chemical pollutant potential to the environment by vaporization has shown that this hazard is essentially nonexistent. Pollution by wind-whipped spray or runoff are determined by the quality of the supernate and can be as contaminated as system liquor or as benign as rainwater. In the case of runoff, suspended solids may be a more critical pollutant than dissolved solids, especially for untreated water.

By far, the most persistent pollution potential is by water percolation through the sludge and subsoil into the subterranean water table. The severity of the pollution is dependent upon both the quantity and quality of the leachate from the disposal sites. Leachate quality was determined by laboratory experimentation by leaching column tests.

Results from these tests show that the concentration of all chemical species decreases continually in the leachate, initially at a high rate and after the displacement of 3 to 5 pore volumes, the rate of decrease is typically very low or the concentration becomes constant. The initial high rate of decrease is believed to be a consequence of a flushing mechanism; the constant or low-rate segment appears to be the consequence of the solubility of crystalline phases.

Chemical treatment of a waste by fixation processing produces a leachate with concentration values of major species nominally one half of untreated sludge at all equivalent leachate volumes. Highly soluble chemical species like sodium and chloride ions are removed effectively from the system in the initial pore flushing. After approximately 5 PVD, the TDS consist primarily of calcium sulfate ions. The results from these tests are presented for TDS in Figure 6, in which all values are normalized to the initial concentration of leachate for untreated sludge. The shapes of these leachate curves are representative of all major chemical species, i.e., calcium, sodium, chloride, sulfate, and sulfite ions. The chemical oxygen demand is directly related to sulfite ion concentration. It has shown an initial value as high as 70 mg/ℓ and attains a steady-state value at about 7 mg/ℓ in anaerobic leachate. The oxygen demand criteria for fisheries in most states is in the range of 4 to 6 mg/ℓ.

Chemical treatment did not reveal a discernible difference from untreated material for trace elements. In most cases, all trace element content in the leachate dropped below detection levels after the initial flushing. In the remaining cases, only lead, zinc, and selenium were found to persist at concentration levels significantly above background, and this finding was independent of chemical treatment.

4.4.2 Alternative Disposal Techniques

The methods by which FGD waste may be disposed will be determined by the environmental acceptability of the waste and the cost of waste

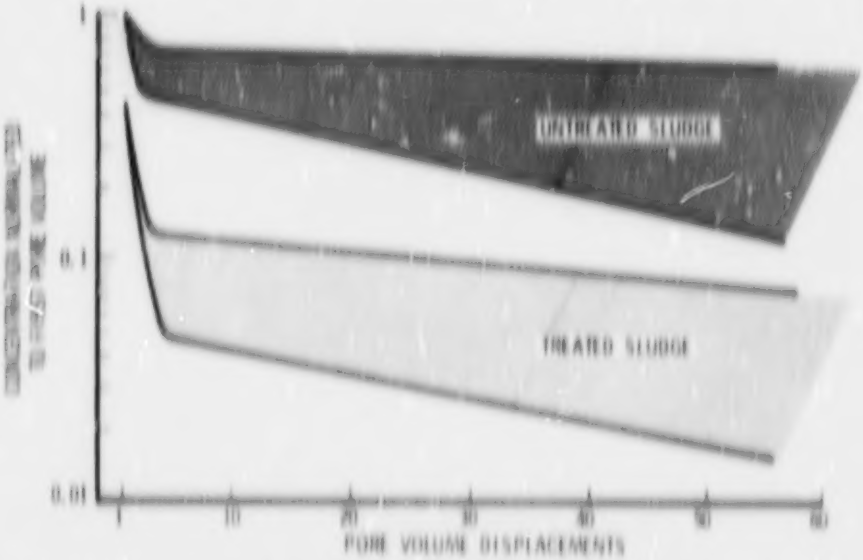

Figure 6. Leachate TDS from treated and untreated sludge as a function of PVD.

disposal. In addition, methods already used in fly ash disposal or in the disposal of other industrial wastes may be used in preference to new or untried techniques. Thus, sludge sluicing to a pond is considered a viable method but may require a pond liner in the event that environmental pollution may otherwise occur. An alternative to ponding is the technique whereby the sludge is sluiced to the disposal basin, but instead of supernate liquor collection the disposal basin is underdrained so that excess liquor can be returned to the scrubber while enhancing structural properties and minimizing seepage by (a) eliminating the supernate hydraulic head and (b) interrupting the internal head via the underdrain mechanism (see Section 9.3.2 for other effects). This method may be preferred in some cases with respect to pollution, costs, and ultimate disposal site disposition.

In the case of chemically treated waste, it is possible to dispose of the waste in a manner resembling ponding, similar to the Pennsylvania Power Company's Bruce Mansfield Station disposal operation. Monitoring of local streams is necessary because of the seepage caused by the constant hydraulic head of the impounded water.

An alternative method for disposal of untreated waste uses a filter or centrifuge to provide a material that can be transported and placed by truck transfer. While transportation costs for this method are intrinsically high, the method offers advantages that offset trucking costs. Particular attention to structural stability may be necessary in this method.

Chemical treatment of FGD wastes provides an additional assurance of environmental acceptance, but the material must be placed in a disposal site in a manner consistent with sound disposal practices. This method is the most expensive among the various disposal alternatives but may be necessary in certain cases where structural stability or environmental protection might otherwise be compromised.

4.4.3 Assessment of the Pollution Potential

On the basis of the laboratory data obtained in this study, an assessment was made of the relative pollution potential of the various alternative methods for FGD waste disposal. Of the routes by which pollutants can enter the environment from a disposal site, it is considered that the most serious method is by percolation of rainwater through the waste and the contamination of groundwater from the dissolved chemical species carried by the recharge.

From the quality of leachate and the permeability rate of water through the waste, the yearly mass loading to the subsoil below each type of disposal site was determined from the site conditions described in Table 6, and these data are plotted in Figure 7. Cases 1 and 3 are for untreated FGD

TABLE 6. INPUT DATA FOR STUDY CASES

Case	Disposal Method	Surface Water	FGD Waste, 5-Year Fill			
			Waste Condition	Depth, ft	Permeability, cm/sec[b]	Fractional Pore Volume
1	Lake[a]	Constant supernate	Untreated	30	10^{-4}	0.67
2	Lake[a]	Constant supernate	Treated	30	10^{-5}	0.67
3	Pond	10. in./yr recharge	Untreated	30	10^{-4}	0.67
4	Pond	10. in./yr recharge	Treated	30	10^{-5}	0.67
5	Landfill	1 in./yr recharge	Treated	30	10^{-5}	0.67

[a] Assumed maximum hydraulic head of 6 ft during filling, including depth of wastes; 1 ft constant water cover thereafter.

[b] For all cases, subsoil permeability = 10^{-5} cm/sec.

waste disposed in a pond. Case 1 has a constant hydraulic head, whereas in Case 3 the water that is available for recharge is only the net from rainfall after evaporation. Cases 2 and 4 are for treated FGD waste disposed and are managed as in Cases 1 and 3, respectively. Case 5 is for treated waste disposed in a landfill in a manner such that only one inch per year is allowed to recharge because of the disposal site design that maximizes runoff. Cases similar to Case 5 are also possible for untreated sludge which may or may not be oxidized to gypsum, dewatered, and placed in a landfill. In these cases, mass loading may be as great as that in Case 3 or as low as that in Case 5, depending upon disposal methods. Generally, the mass of TDS that passes through the subsoil varies by a factor of 100 between ponding untreated waste and landfilling chemically treated waste.

4.5 DISPOSAL COST ESTIMATES

Cost estimates for ponding and fixation landfilling have been made and reported by Aerospace on several occasions. During recent studies associated with the EPA Shawnee field disposal evaluation project, Aerospace cost estimates were made of fixation disposal and were reported in the initial report on that study (2). The Aerospace estimates for lined-pond costs, which were presented in the initial report on our sludge disposal study (1) and

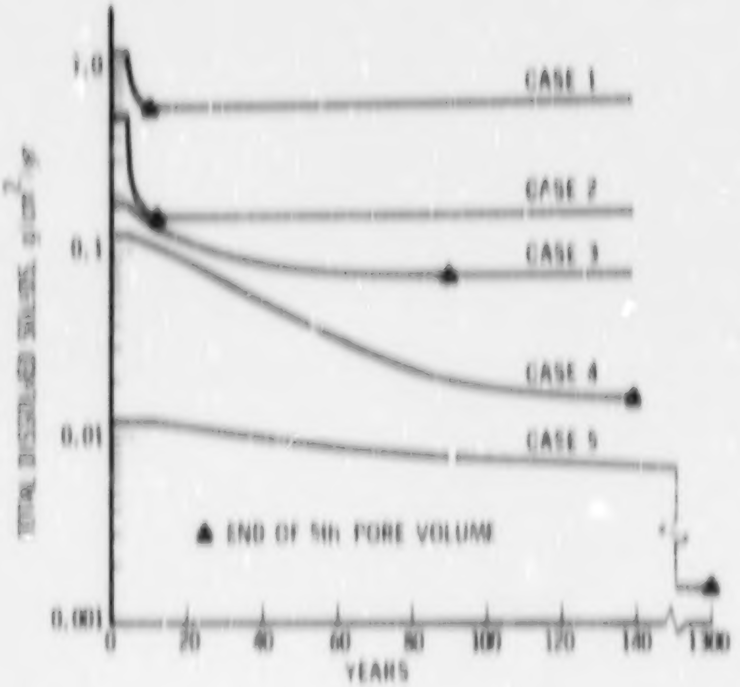

Figure 7. Mass loading of TDS to subsoil for various disposal modes of treated and untreated FGC wastes.

at the EPA 1974 Flue Gas Desulfurization Symposium in Atlanta (5), are updated in this report to January 1976 costs. A summary of these costs estimates is presented in Table 7, and a discussion o' the study is given in Section 10.2.

TABLE 7. SLUDGE DISPOSAL COST RANGES (UNTREATED AND CHEMICALLY TREATED LANDFILLS, 1000-MW STATION, 50 PERCENT LOAD FACTOR, 30-YEAR AVERAGE, JANUARY 1976 DOLLARS)

Disposal Method	Base Material	\$/Ton Sludge[a, b] (Dry)	\$/Ton Coal[b]	Mills/kWh[b, c, d]
Untreated				
Pond	Natural Clay[e]	3.50	1.00	0.4
Pond	Liner[f]	5.70-7.80	1.60-2.20	0.7-1.0
Chemically Treated[g]	Indigenous Soil	7.30-11.40	2.10-3.20	0.9-1.4

[a] 510,000 short tons/year average (dry basis) including fly ash.

[b] Coal burned at rate of 0.88 lb/kWh, 3% sulfur, 12% ash, 85% SO_2 removal, 1.2 $CaCO_3/SO_2$ mole ratio.

[c] Land costs at \$1000/acre are included (equivalent to \$0.25/ton sludge, dry).

[d] Disposal within 5 miles of power plant.

[e] Assumes coefficient of permeability of clay is 1×10^{-6} cm/sec or better.

[f] Ponding costs cover range based on low-to-high material costs, i.e., PVC-20 (low) to Hypalon-30 (high).

[g] Chemical fixation costs vary, depending on characteristics of the waste and the disposal process chosen.

SECTION V

DISPOSAL CRITERIA

This study is directed toward the determination and evaluation of environmentally acceptable methods for land disposal, with emphasis on landfilling and ponding. Ocean and mine disposal alternatives are being investigated in other EPA-sponsored studies (3) using applicable materials characterization data from this and other programs. Therefore, disposal criteria applicable to this study are restricted to the quality of groundwater and surface water affected by flue gas desulfurization (FGD) waste waters by means of seepage or runoff and to the structural quality of the waste material as it applies to subsequent disposal site reclamation. Currently, there are no criteria that are specifically applicable to land disposal methods that could provide direct guidelines to the acceptability of FGD waste disposal methods. However, at this time, EPA is conducting studies to establish a data base for the development of appropriate standards for the disposal of these wastes (3).

5.1 DISPOSAL ALTERNATIVES FOR FGD WASTE

Whereas the lack of appropriate disposal criteria prevents a direct evaluation of specific disposal methods relative to limiting standards, it is possible, nevertheless, to evaluate the relative merit of currently used and proposed methods of disposal. Although many variations of disposal may be used, the most practiced generalized alternatives currently available can be summarized as disposal of wastes in (a) ponds, (b) basins, or (c) landfills. In all cases, closed-loop scrubber systems are assumed (11), and direct discharge of scrubber liquors or untreated wastes to streams is not considered. Ponding is a method by which the waste is sluiced to the disposal site and supernate returned to the scrubber. Basin disposal is defined here as a method of disposal in a closed site where runoff is contained; additionally, it is presumed that an underdrainage system is incorporated so that excess waters can be returned to the scrubber. A landfill is defined here as an open site where runoff is not contained within the site. The general categories of disposal and the considerations required for environmental control are shown in Table 8.

5.2 ENVIRONMENTAL EFFECTS OF FGD WASTE DISPOSAL ALTERNATIVES

5.2.1 Rainwater Seepage

In each case, seepage of rainwater through the waste and eventual contamination of groundwater pose an environmental concern for all disposal

TABLE 8. ENVIRONMENTAL EFFECTS OF DISPOSAL ALTERNATIVES

Type of Disposal	Condition of Waste	Primary Drainage	Environmental Effects		
			Seepage	Runoff	Land Reuse
Pond	Untreated[a] or	Supernate	Yes	No	No
	chemically fixed[b]	Supernate	Yes	No	Yes
Basin	Untreated[a] or conditioned[c]	Underdrainage	Yes	No	No
Landfill	Conditioned[c] or chemically fixed[b]	Runoff	Yes	Yes	Yes

[a] Untreated waste refers to FGD sludges as emitted from primary or secondary dewatering equipment

[b] Chemically fixed sludges refer to the waste treated by one of several commercial processes that make these wastes suitable for landfill disposal.

[c] Conditioned waste refers to sludge treated by techniques other than chemical fixation and includes oxidation to gypsum and dewatering by mixing with dry fly ash or other agents that allow the material to be handled in a manner similar to that for soils.

methods. Runoff is a potential source of environmental pollution for landfill sites because, by definition, these sites are open and do not necessarily return water to the scrubber. Only in the case of ponding is it clear that the disposal site is not directly amenable to land reclamation efforts, although even in some of these cases it may be possible upon retirement to air-dry, cap, and vegetate the site.

Ultimately, federal or state regulations will apply as a result of the Resource Conservation and Recovery Act, PL 94-580, 21 October 1976 (15), which gives EPA the authority to regulate wastes from air pollution control devices. In the absence of federal standards for FGD waste disposal, existing criteria were examined to establish a basis on which appropriate regulations may be promulgated. The federal regulation that most nearly relates to a limit on seepage water quality is the EPA's "Alternative Waste Management Techniques for Best Practical Waste Treatment" (14). These criteria apply to public-owned treatment and land application of waste water. Relevant excerpts from these criteria are as follows:

The ground water resulting from the land application of wastewater, including the affected native ground water, shall meet the following criteria:

Case I: The ground water can potentially be used for drinking water supply.

(1) The maximum contaminant levels for inorganic chemicals and organic chemicals specified in the National Interim Primary Drinking Water Regulations (40 CFR 141) (Appendix D) for drinking water supply systems should not be exceeded except as indicated below (see Note 1).

(2) If the existing concentration of a parameter exceeds the maximum contaminant levels for inorganic chemicals or organic chemicals, there should not be an increase in the concentration of that parameter due to land application of wastewater.

Case II: The ground water is used for drinking water supply.

(1) The criteria for Case I should be met.

(2) The maximum microbiological contaminant levels for drinking water supply systems specified in the National Interim Primary Drinking Water Regulations (40 CFR 141) (Appendix D) should not be exceeded in cases where the ground water is used without disinfection (see Note 1).

Case III: Uses other than drinking water supply.

(1) Ground water criteria should be established by the Regional Administrator based on the present or potential use of the ground water.

The Regional Administrator in conjunction with the appropriate State officials and the grantee shall determine on a site-by-site basis the areas in the vicinity of a specific land application site where the criteria in Case I, II, and III shall apply. Specifically determined shall be the monitoring requirements appropriate for the project site. This determination shall be made with the objective of protecting the ground water for use as a drinking water supply and or other designated uses as appropriate and preventing irrevocable damage to ground water. Requirements shall include provisions for monitoring the effect on the native ground water.

APPENDIX D
GROUND WATER REQUIREMENTS

The following maximum contaminant levels contained in the National Interim Primary Drinking Water Regulations (40 CFR 141) are reprinted for convenience and clarity. The National Interim Primary Drinking Water Regulations were published in final form in the Federal Register on December 24, 1975. In accordance with the criteria for best practicable waste treatment, 40 CFR 141 should be consulted in its entirety when applying the standards contained therein to wastewater treatment systems employing land application techniques and land utilization practices.

Maximum contaminant levels for inorganic chemicals. The following are the maximum levels of inorganic chemicals other than fluoride:

Contaminant:	Level (milligrams per liter)
Arsenic	0.05
Barium	1.
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10.
Selenium	0.01
Silver	0.05

The maximum contaminant levels for fluoride are:

Temperature degrees Fahrenheit[1]	Degrees Celsius	Level (milligrams per liter)
53.7 and below	12 and below	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

[1] Annual average of the maximum daily air temperature.

Essentially, these criteria state that the groundwater, resulting from land applications of waste water, shall be limited to the maximum contaminant levels contained in the "National Interim Primary Drinking Water Regulations" (NIPDWR) (13) or to the existing concentration if the latter is greater. If the groundwater is to be used for other than a drinking water supply, "the ground water [*sic*] criteria should be established by the Regional Administrator, . . ." In contrast to the "United States Public Health Service [USPHS] Drinking Water Standards, 1962" (15), which limit sulfate and chloride to 250 mg/ℓ each, no limits are given in the NIPDWR for sulfate or chloride; however, these and other substances may be included in secondary standards, when issued.

It is apparent that water quality criteria are not finalized when it is considered that (a) sodium, sulfate, chloride, copper, zinc, and other substances do not appear in the NIPDWR and are undergoing further study (see following excerpts) and (b) the groundwater resulting from land application of waste water is required to meet the criteria for NIPDWR, whereas the maximum contaminant levels (MCL) specified in the NIPDWR (except for turbidity) apply to water at the consumer tap. The following excerpts provide some insight into relevant background considerations in the development of water criteria.

a. Excerpts from NIPDWR (12):

13. Sodium. Several comments suggested the possibility of an MCL for sodium and the National Drinking Water Advisory Council recommended that consideration be given to monitoring for sodium so that the public can be informed of the sodium content of available water. These concerns result from the fact that many persons in the United States suffer from diseases which are influenced by dietary sodium intake. In addition, persons may wish to limit their sodium intake for other reasons. However, EPA has not proposed an MCL for sodium, and the Advisory Council did not recommend an MCL, because the data available do not support any particular level for sodium in drinking water, and because regulation of sodium by an MCL is a relatively inflexible, very expensive means of dealing with a problem which varies greatly from person to person.

EPA has requested the National Academy of Sciences to include sodium in its study of the health effects of inorganic chemicals. In the meantime, the Agency recommends that the States institute monitoring programs for sodium, and that physicians and consumers be informed of the sodium concentration in public water systems so that they can take action they may consider appropriate.

14. Sulfate. Comments also were submitted urging the adoption of an MCL for sulfate. As in the case of sodium, the National Drinking Water Advisory Council recommended monitoring for sulfate levels, but did not recommend the adoption of a maximum contaminant level.

The sulfate question is similar to the sodium question in that available data do not support the establishment of any given level. A relatively high concentration of sulfate in drinking water has little or no known effect on regular users of the water, but transients using high sulfate water sometimes experience a laxative effect. Whether this effect will occur, and its severity, varies greatly with such factors as the level of sulfate in the water being consumed and the level of sulfate to which the transient is accustomed. EPA recommends that States institute monitoring programs for sulfates, and that transients be notified if the sulfate content of the water is high. Such notification should include an assessment of the possible physiological effects of consumption of the water.

The National Academy of Sciences has been asked to consider sulfate in its study. An MCL for sulfate will be proposed if it is supported by the available data.

POINT OF MEASUREMENT

Other comments on maximum contaminant levels focused on the proposed requirement that such levels be tested at the consumer's tap. Concern was expressed over the inability of the public water system to control potential sources of contaminants which are under the control of the consumer.

The promulgated definition of "maximum contaminant level," § 141.2(c), retains the requirement that the maximum contaminant level be measured at the tap except in the case of turbidity, which should be measured at the point of entry to the distribution system. However, the definition has been expanded to make clear that contaminants added to the water by circumstances under the control of the consumer are not the responsibility of the supplier of water, unless the contaminants result from corrosion of piping and plumbing resulting from the quality of the water supplied. It should be noted, however, that this requirement should not be interpreted as to discourage local, aggressive cross connection control measures.

b. Excerpt from McKee and Wolf (17):

> CHLORIDES
>
> a. Domestic Water Supplies. Chlorides in drinking water are generally not harmful to human beings until high concentrations are reached, although chlorides may be injurious to some people suffering from diseases of heart or kidneys. Restrictions on chloride concentrations in drinking water are generally based on palatability requirements rather than on health.
>
> Chlorides in water may impart a salty taste at concentrations as low as 100 mg/ℓ, although in some waters 700 mg/ℓ may not be noticeable (see also Tastes). According to the Kettering Laboratory, the most taste-sensitive people can detect chloride from calcium salts at 96 mg/ℓ and from sodium salts at 121 mg/ℓ (based on work by Whipple). For average individuals, the taste threshold is about 400 mg/ℓ. Lockhart et al. reported the taste thresholds of NaCl, KCl, and $CaCl_2$ to be 345, 650, and 347 mg/ℓ, corresponding to chloride concentrations of 210, 310, and 222 mg/ℓ respectively. The fact that a taste is detectable, however, does not mean that it is objectionable; indeed, many people prefer water that is partly mineralized to the flat taste of distilled water.
>
> The tolerance of chlorides by human beings varies with climate and exertion, and chlorides lost through perspiration may be replaced by chlorides in either the diet or drinking water. From hot dry areas have come reports that chloride concentrations up to almost 900 mg/ℓ have not been harmful, and Rudolfs maintains that even 1000 mg/ℓ is harmless. According to a Kettering Laboratory survey, laxative effects of chloride are generally apparent only when an individual has been accustomed to a lower concentration of the salt. Within a few days, an individual adjusts physiologically to a higher level of salt intake. In general, it is the cation (calcium, magnesium, sodium, or potassium) associated with the chloride that produces a harmful effect. It has been reported in Russia that under conditions of artificially induced thirst, test subjects drank 30-60 percent less water containing 1000 mg/ℓ of chloride than they did of tap water.

Essentially, these excerpts as applied to land application of waste water state that for those chemical species which FGD waste is most likely to generate as a pollutant, i.e., sodium, sulfate, and chloride, there currently exist no primary maximum contamination levels, but suggest that such limits may be subsequently proposed, probably as secondary standards, if they can be supported by the available data. It is presumed that similar criteria will be promulgated for control of FGD waste waters and that sodium, sulfate, and chlorides will be subject to similar considerations. In the absence of federal regulations for FGD waste, it may be prudent to anticipate that at least one of these species will be regulated and that, in controlling the maximum contaminant level of one, the other two are likely to be similarly controlled.

Because sludge is not discharged to streams and since chemical oxygen demand (COD) is significant only for fresh liquor (Table 9), it is not considered here. One of the difficulties in applying existing water standards to FGD waste waters is that they apply to the quality of the groundwater or tap water and do not directly define the quality of seepage waters from a FGD waste

TABLE 9. CHEMICAL CONSTITUENTS IN LEACHATE FROM UNTREATED AND CHEMICALLY TREATED FGD WASTE AFTER 1 and 50 PORE PVD (CONCENTRATIONS IN mg/ℓ)

Chemical Constituent	Untreated Waste		Treated Waste	
	1st PVD	50th PVD	1st PVD	50th PVD
Arsenic	0,02	0,004	0,015	<0,004
Beryllium	0,01	<0,004	0,008	<0,002
Cadmium	0,015	0,002	0,02	0,002
Chromium	0,045	<0,003	0,06	0,003
Calcium	0,045	0,010	0,025	0,005
Lead	0,25	0,010	0,15	0,03
Mercury	0,0005	<0,00005	0,0007	0,0002
Selenium	0,055	0,006	0,040	0,008
Zinc	0,65	0,04	0,27	0,03
Chloride	2600	100	600	75
Fluoride	4,0	0,8	1,1	0,4
Sulfite	50	30	15	20
Sulfate	6500	1200	3500	450
Total Dissolved Solids	10,000	2200	6000	1000
Chemical Oxygen Demand	10	6	7	4
pH	6,6	5,5	6,8	8,0

disposal site. Nevertheless, possible approaches to meet existing standards, either individually or in combination, are as follows:

a. Eliminate seepage by using impermeable liners or by collecting and recycling all seepage.

b. Account for attenuation via adsorption or cation exchange in underlying soil.

c. Force-mix seepage with groundwater for dilution.

d. Mix seepage and groundwater with connecting streams.

e. Chemically reduce solubility and/or permeability and mix with groundwater.

f. Chemically reduce solubility and/or permeability and reduce or eliminate seepage by maximizing runoff.

The selection of techniques to accommodate anticipated standards for groundwater quality as a consequence of FGD waste seepage will depend on climatological, geological, and hydrological considerations of the disposal site as well as the quality of leachate that emits from the site. Typical concentrations of leachate from untreated and chemically treated sludges are given in Table 9. Total mass loading to groundwater as determined from concentration and permeability measurements will determine the impact on the groundwater. Permeability coefficients can vary over several orders of magnitude and depend on the specific properties of sludges and the methods by which the sludge is placed into the disposal site.

5.2.2 Landfill Runoff

The previous discussion has addressed the prevention of pollution from rainwater seepage through a disposal site. For the landfill method of disposal, runoff is a major concern for environmental control. For those cases where runoff is allowed to inundate adjacent flatland through which it may permeate, the regulations promulgated for seepage would be applicable. For other cases where runoff is directed to receiving streams, the most applicable regulations would be state stream standards. Thus, where the receiving stream size is small relative to water supplied to the stream by landfill runoff, the prevention of stream contamination may be a primary environmental concern. As in the case of seepage, the method selected for the prevention of pollution will be determined by the quality of runoff waters. Possible approaches for the prevention of stream contamination are as follows:

a. Collect all runoff in lined siltation ponds.

b. Cover and vegetate landfill so that runoff water quality is not contaminated by the FGD waste.

c. Force-mix runoff waters with stream waters.

d. Divert runoff to flatland where evaporation and seepage can take place.

e. Dilute landfill runoff with runoff from other sources before emitting to streams.

Selection of any of these alternatives will be dependent upon site-specific considerations.

5.2.3 Land Reuse

In addition to chemical contamination prevention, environmental concern also includes the attainment of certain structural qualities if the site is to be reclaimed. In the absence of specific criteria, a conservative value of 1.8 kg/cm² (25 psi) minimum unconfined compressive strength was considered because it could be met on the basis of the following observations:

a. Heavy equipment on tires carrying 45 psi have repeatedly driven onto a saturated, fixed pond at the TVA Shawnee field evaluation site (2), maintained traction, and left only a mild track in the material. This material has an unconfined compressive strength of 27 psi in a wet condition.

b. All chemically treated wastes studied attained and usually exceeded this strength.

c. Sulfite wastes oxidized to gypsum attain this strength at a solids content of about 65 percent.

d. Sulfite wastes attain this strength at a solids content of about 70 percent.

e. The standard test for unconfined compressive strength is simple and inexpensive.

Studies are continuing in this program to relate disposal site strength to confined compressive strength criteria and to include untreated sludges that attain a degree of strength through dewatering.

5.3 SELECTION OF DISPOSAL CRITERIA

It has been demonstrated that disposal methods exist by which anticipated chemical and structural criteria can be met. Simply stated, if reclamation of the land is not required, ponding in a naturally impermeable or lined basin is adequate. If structural characteristics are required, chemical fixation of the material and placement in an impermeable basin would certainly provide adequate strength and would not allow seepage to groundwaters. Moreover, a lined siltation pond can assure environmental protection from any runoff waters. However, these solutions may be overly conservative and incur costs far beyond that necessary to meet expected criteria.

Demonstrations, both small-scale and operational, of fixed and conditional waste landfills (without liners) are now in progress and should verify the environmental acceptability of such sites when managed to prevent the collection of water on the surface and, thereby, the elimination of hydraulic heads and subsequent seepage. Runoff is collected in a siltation pond where suspended solids settle and are periodically dredged and returned to the fixation process. One operational fixed waste disposal site allows surface water. Its environmental acceptability is partially based upon the mixing of supernate with a nearby stream and a connecting river. All sites are monitored for water quality.

It is apparent that each disposal site and the material placed in it have individual characteristics different from most others. These include waste material properties, weather, topography, soil characteristics, and nearby stream quality and flow characteristics. Therefore, the disposal method chosen for any site will generally be selected on site-specific conditions. Because of this, the establishment of a single criterion for all cases may be impractical.

At this time, studies are continuing in this program, other EPA projects, and in industry to define and evaluate environmentally sound, least-cost methods of waste disposal, covering the range of ponding; dewatering, mixing with fly ash and compacting; conversion to gypsum and dewatering; and chemical fixation. Data from these studies are expected to provide a base from which an appropriate disposal mode may be selected for any given site. In addition, the EPA is reviewing local regulations on a national scale to identify applicable regulations and to determine whether they will permit the disposal of treated and untreated flue gas cleaning (FGC) wastes. Because of the wide variations in the characteristics of wastes, weather, soils, topography, and groundwater from site to site, permits are currently being awarded on a site-specific basis. Eventually, state regulations will apply as a result of the "Resources Conservation and Recovery Act of 1976" (13), but these regulations will not be enacted until federal standards are promulgated.

A detailed discussion of disposal and environmental relationships and the methodology of alternative disposal techniques is given in Section IX.

SECTION VI

PHYSICAL PROPERTIES DETERMINATION

6.1 BACKGROUND

The disposal, handling, and transportation techniques that will be applied to flue gas desulfurization (FGD) wastes will be strongly dependent upon the physical behavior of these wastes and the resultant costs. The physical properties of FGD wastes that limit or restrict the applicability of certain techniques include the degree of solids content, crystalline phase composition, particle size, and distribution. Experimental tests were conducted to characterize the FGD wastes of seven power plant scrubbing facilities,[*] including pilot, prototype, and full-scale scrubber units ranging from 1- to 125-MW equivalent capacities. In each case, the FGD waste studied was the waste material for each facility, received in its normal state of disposal. Although recognition was given to the potential that some waste materials may be suitable for use in specific commercial applications (1), the tests were directed toward the use of FGD wastes in landfilling and land reclamation applications. The potential for commercial application of FGD waste at present represents a limited quantity of material, and the required knowledge of specific physical properties is strongly dependent upon the particular application. In contrast, the major applications for these wastes are in landfilling and land reclamation, where the physical properties required are well known.

The technologies for transporting, handling, and disposal of fly ash have evolved over many years of electrical power production; to the extent possible, it appears that these technologies will be extended to FGD wastes as well. Two important differences exist, however: (a) The quantity of FGD wastes that will be produced exceeds fly ash production; and (b) whereas environmental controls on the disposal of fly ash have been somewhat limited the disposal of FGD wastes must be done in an environmentally acceptable manner. Thus, the technologies used for fly ash must be investigated relative to their environmental impact when applied to FGD wastes. Moreover, since FGD wastes characteristics differ, both physically and chemically from fly ash characteristics, their suitability in specific applications must be evaluated under the various conditions in which they are expected to be disposed.

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[*] A complete description of the power plant scrubbing facilities of each unit and test samples is given in Appendix B.

The physical parameters investigated include specific gravity, bulk density as a function of solids content, water retention for particular dewatering techniques, viscosity of slurries at various solids content, permeability as a function of particle packing fraction (converse of void fraction), compactability as a function of solids content, and strength as a function of solids content. The following subsections describe the tests conducted and present the results for each of the FGD wastes investigated. Wherever possible, the effects of fly ash are shown.

In addition to FGD waste disposal in an untreated state, the option exists to condition or chemically treat FGD waste materials by a number of alternative methods. Such treatment necessarily increases the unit disposal cost, but renders these materials more environmentally acceptable. Selected tests of physical properties have been conducted on chemically treated FGD wastes to determine both environmental acceptability and physical behavior as related to handling and structure in land reclamation applications.

6.2 SOLIDS CHARACTERIZATION

The physical properties of any liquid-solid mixture are dependent upon the characteristics of both the liquid and the solid constituents as well as the interaction between them. The FGD wastes are such mixtures and contain four principal crystalline phases: calcium sulfite hemihydrate, calcium sulfate dihydrate, fly ash, and unreacted lime or limestone (usually appearing as calcium carbonate by reaction with atmospheric CO_2). These solid phases exist as small crystals suspended in an aqueous liquor which is usually in equilibrium (saturated) with these solids. In addition, sodium chloride or calcium chloride is present as totally dissolved salts. A complete chemical characterization of each FGD system liquor is given in Appendix D.

The relative amounts of each of the solid crystalline phases is dependent upon the system design parameters: the sulfur content of the coal used, efficiency of SO_2 scrubbing, fly ash in the flue gas entering the scrubber, efficiency of the system to remove fly ash, stoichiometric ratio of absorbent relative to sulfur content, absorbent utilization efficiency, and amount of oxidation of the sulfur products that takes place in the scrubber system. The efficiency of scrubbing SO_2 and fly ash from the flue gas and the amount of sulfur product oxidation that takes place are primarily functions of system design, but other factors enter into these processes, e.g., combustion behavior in the boiler, nature of mineral phases in the coal and its total ash content, reactivity of lime or limestone, and particle size and distribution of the sulfite particles. The independent and interdependent variables that affect the composition and characteristics of the resulting waste product are so numerous and varied that it is not likely that any two sulfur waste products are identical. Further, each crystalline phase with its specific characteristics has an influence on the behavior of the sludge. Characterization of the solids portion of each sludge studied relative to phase identification and particle characteristics is discussed in Appendix A. To the extent possible, correlations between the particular characteristics of these phases and behavior of the sludge are made in subsequent subsections.

6.3 VISCOSITY

The existing technology for transporting fly ash to a disposal site often includes sluicing the fly ash with waste waters. An option for transporting FGD wastes to a disposal site is similar in method; i.e., the waste is pumped in an as-produced condition as a slurry or sludge.

The viscosity of the liquid waste is a direct measure of its pumpability, which affects the cost of transportation as well as system design. For example, if upon dewatering the liquid waste the viscosity is affected adversely in a way that precludes the pumping of the waste to the disposal site, the system may be designed so that the dewatering operation is performed at the disposal site. This approach can be applied to either primary dewatering (clarifier, thickener) or secondary dewatering (filter, centrifuge).

Waste materials produced in FGD systems contain finely divided solids suspended in a water system. Sulfur waste products (both sulfate and sulfite) tend to have particle sizes typically in the same range as fly ash, between 100 and 1 µm. Whereas fly ash is produced as spheres, sulfur wastes are either platey or rosettes, as sulfite, or blocky, as sulfate. In addition, unreacted limestone (or lime) is usually present in the waste and contributes an additional shape parameter. The particle shape, particularly for the sulfite, is the cause of the water retention nature previously observed in FGD waste (1). In addition, fly ash when present in FGD wastes can provide a marked measure of fluidity that the sludge would not otherwise have. (One of several reasons for adding fly ash to concentrate mixes as a replacement for cement is to increase pumpability.) The sulfite and fly ash work in opposition to each other in promoting pumpability, but factors other than shape affect viscosity. These include solids content, particle size, and particle size distribution. Thus, the property of viscosity is a function of a multitude of parameters and is not sufficiently understood so that behavior can be predicted from a knowledge of these parameters; therefore, measurement of this property becomes necessary.

6.3.1 Experimental Procedure

The viscosity measurements were performed at room temperature using a rotating cup viscometer[*] having a cylindrical sleeve immersed in the FGD fluid waste and rotating at 64 rpm. The 2.4-cm (15/16 in.) diameter rotating sleeve generates a shear rate of 7.9 cm/sec (15.6 ft/min) at its outer surface. The range of viscosities that can be measured with this sleeve is 3 to 150 poise. (Water has a viscosity of 0.01 poise.)

Prior to measurement, the solids content of the sludge was adjusted to the desired value, and the mixture was homogenized by hand stirring. The cylindrical sleeve was then immersed in the sludge and left undisturbed for 15 sec, during which time the stirring motion ceased. The viscometer was then turned on, and the viscosity was noted.

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[*] Model VT-02, R and A Products Co., Brooklyn, N.Y.

6.1.2 Viscosity Test Results

The viscosity of FGD sludges from seven power plants as a function of water content is presented in Figure 8. Sludge from the Tennessee Valley Authority (TVA) Shawnee Station turbulent contact absorber (TCA) scrubber was tested from samples taken on three occasions. The results show that, among the sludges tested, pumpable mixtures (≤20 poise) ranged from a high solids content of 70 percent for the Arizona Public Service (APS) Company Cholla sample to a low solids content of 32 percent for both the Utah Power and Light (UPL) Company Gadsby Station and the General Motors (GM) Chevrolet-Parma Power Plant samples. From this wide spread, the importance of experimentally determined data for system design parameters becomes clearly evident.

The relative position of each curve presented in Figure 8 may be rationally explained, but certain anomalies nevertheless exist for nearly every attempt at fully understanding this behavior. The position of the APS Cholla sludge at high solids content can be attributed to the high concentration of fly ash (nearly 60 percent) in the sludge and also possibly to the presence of large blocky sulfate particles, which constitute the major fraction of the remaining solids. The UPL Gadsby and GM Parma sludges both had a low fly ash content (7 to 8 percent) and a low solids content. Only the Southern California Edison (SCE) Mohave Generating Station sludge was lower in fly ash content (3 percent), but its position as the second-highest in solids content among the sludges tested appears anomalous. The SCE Mohave sludge solids consisted of large, blocky equiaxial sulfate particles, and it may be the similarity of these particles to spherical fly ash that determined the viscosity of this sludge in relationship to that of other sludges.

The sludge from the TVA Shawnee TCA scrubbing facility was tested on three sampling occasions; the curves 5, 6, and 7 in Figure 8 are nearly parallel but are displaced over a 7 percent solids range (at 20 poise) in the order of highest viscosity for the lowest solids content, again revealing the role of fly ash in increasing fluidity. This sludge was characterized by large, thin, stacked plates of sulfite, and the fly ash particle-size range was broad. The Shawnee venturi sludge (curve 3) was chemically similar to the TCA sludge and had the same particle-size range of fly ash, but the sulfite did not exist as large plates but, predominantly, as rosettes of sulfite platelets or small stacks of plates. It is not understood whether the change in sulfite particle shape was responsible for its relative viscosity since by fly ash content this sludge would be expected to lie between curves 5 and 7.

The Duquesne Light Company (DLC) Phillips Power Station sludge contained predominately large lath-like crystals of sulfate and had a high fly ash content (~60 percent), much like the APS Cholla sludge. On the basis of these variables, the DLC Phillips sludge would be expected to have a viscosity much like the Cholla sludge. The relative position of the Phillips sludge is probably also a consequence of other forces acting within the sludge material,

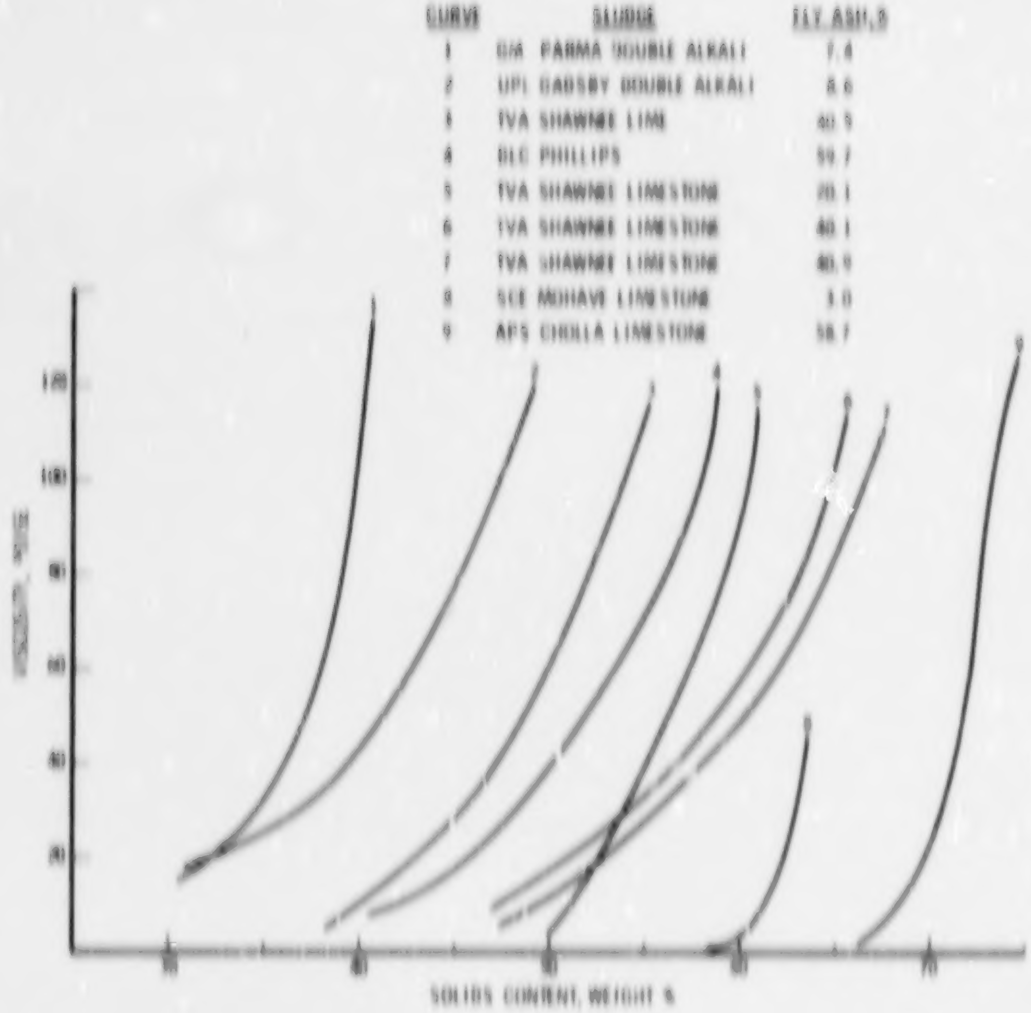

Figure 8. Viscosity of desulfurization sludge.

The slopes of the viscosity curves as a function of solids content lie in two groups: The lower slope group includes all sludges from both TVA Shawnee scrubbers and the UPL Gadsby facility; the higher slope group includes all other sludges. Presently, no parameter has been identified to explain this behavior.

Thus far, the results of viscosity tests suggest that fly ash decreases the viscosity of a sludge. In addition, particle shape, size, and distribution appear to influence viscosity behavior.

6.4 WET BULK DENSITIES

Dewatering of power plant sludge is advantageous for several reasons which are associated with disposal costs and environmental considerations. Because land areas will be used for FGD waste disposal, the decrease in volume that accompanies effective dewatering will minimize the land required for disposal. In many western states where water scarcity often dictates maximum water reuse, the water returned to the scrubbing system reduces the need for fresh makeup water. Further, dewatering minimizes the amount of liquor associated with the solids and thus reduces the pollution potential associated with the potentially high mobility of the liquid phase of wastes; it facilitates handling and reduces fixation costs.

The ability to dewater a sludge is a function of many variables but primarily of the dewatering method used, the size and distribution of particles, and the structure of the particles as determined by crystalline phase. Primary dewatering by clarifiers or thickeners separates water from a slurry principally through the action of gravitational forces. The secondary methods of dewatering typically used are vacuum filtration and centrifugation. In some cases, natural settling may also be considered if the resultant properties and economics are favorable.

The effectiveness of a dewatering operation is best measured by the relative quantity of water that remains with the solid after performing the dewatering operation. The wet bulk density of a sludge is the weight of a unit volume of dewatered sludge containing both liquid and solid phases. The wet bulk density ρ_B of a material can be calculated from the weight fraction solids content f_s, the true density of the solids ρ_s, and the density of water ρ_w by the following equation:

$$\rho_B = \frac{\rho_s \rho_w}{\rho_w f_s + \rho_s (1 - f_s)} \qquad (3)$$

When the amount of water within the sludge samples is lower than the value that represents a point of maximum density where all particles are in contact, the density of the sludge can be calculated by the following equation:

$$\rho_B = \frac{\rho_D}{f_s} \tag{4}$$

The solids content at the maximum density of the sludge is determined by the coincidence of these two expressions and is given as follows:

$$f_{s(max)} = \frac{1}{1 + \rho_w[(1/\rho_D) - (1/\rho_s)]} \tag{5}$$

Thus, the relationship of wet bulk density with solids content can be calculated from only two values, the true density of the solids ρ_s and the dry bulk density of the solids ρ_D.

6.4.1 Experimental Procedure

The wet bulk density was determined on eight FGD sludge samples after each was dewatered by settling, settling with free underdrainage, vacuum filtration, and centrifugation. These determinations were made by measuring the weight and volume of a dewatered sample. Subsequently, the samples were dried to constant weight, and their weight and volume were again determined. From the latter measurements the dry bulk densities were determined, and from the relative change in weight the solids content of the wet sample was determined.

The true density of each solid was measured by a method of air displacement, using a Beckman air pycnometer. The air pycnometer operates on the principle of Boyle's law in which the volume of air displaced by the sample is accurately measured.

6.4.2 Bulk Density Test Results

The wet bulk density of the eight FGD sludges as determined by Equations (3) and (4) is presented in Figures 9 through 16 as solid lines. In addition, the measured wet bulk density of dewatered samples is plotted as datum points on these curves and represent the density obtained by (a) settling in a volumetric flask, (b) settling in a Buchner funnel where the sludge is allowed to drain freely, (c) filtration in a Buchner funnel with vacuum assistance, and (d) centrifugation in a glass vial with a laboratory centrifuge. The right-hand portion of the figures are calculated from Equation (4) and are different for each dewatering method, because the dry bulk density of the solids differs as a consequence of the method of dewatering. This is so

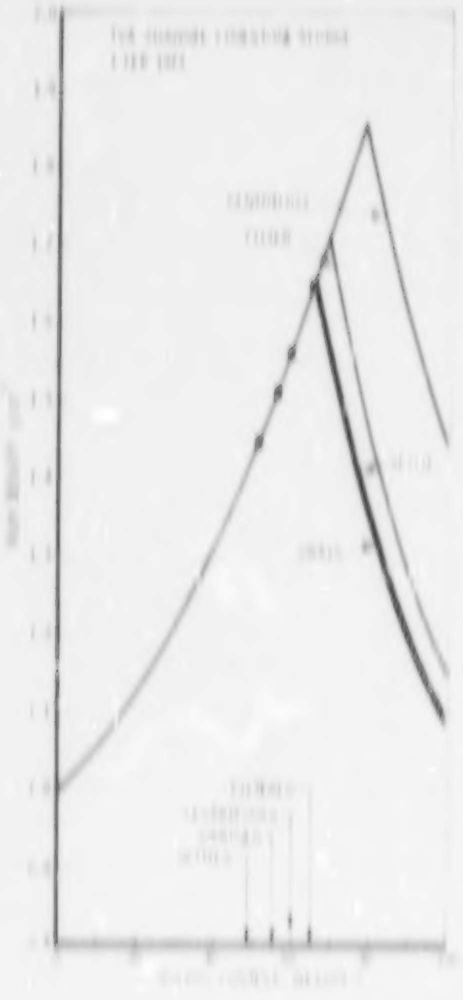

Figure 9. Wet bulk density of TVA Shawnee limestone sludge and dewatered samples: 1 Feb 1973.

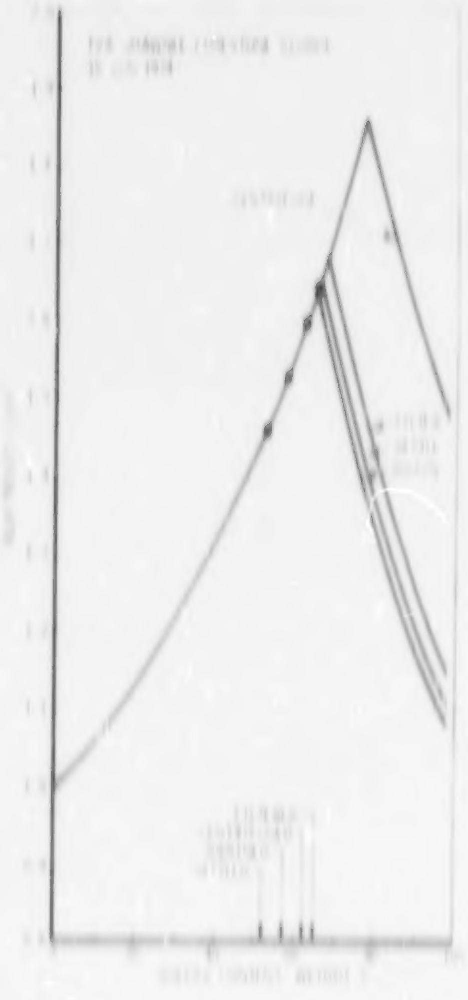

Figure 10. Wet bulk density of TVA Shawnee limestone sludge and dewatered samples: 15 Jun 1974.

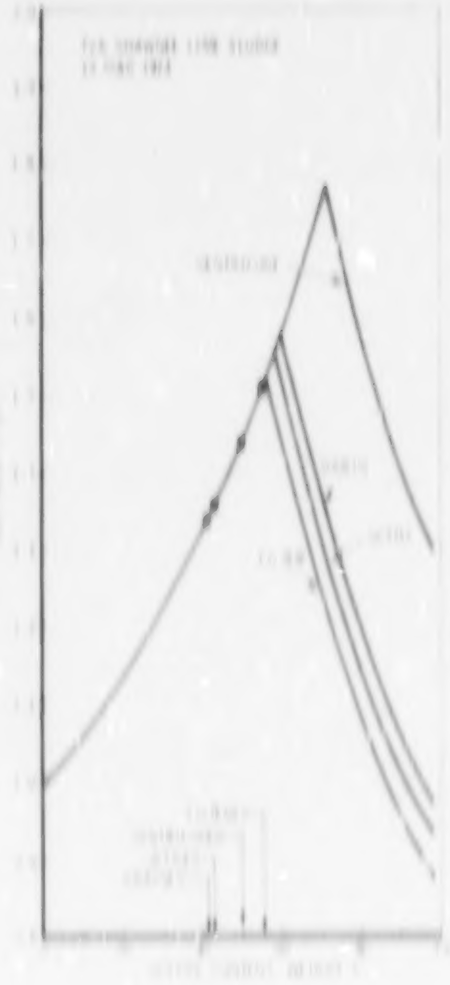

Figure 11. Wet bulk density of TVA Shawnee lime sludge and dewatered samples: 19 Mar 1974.

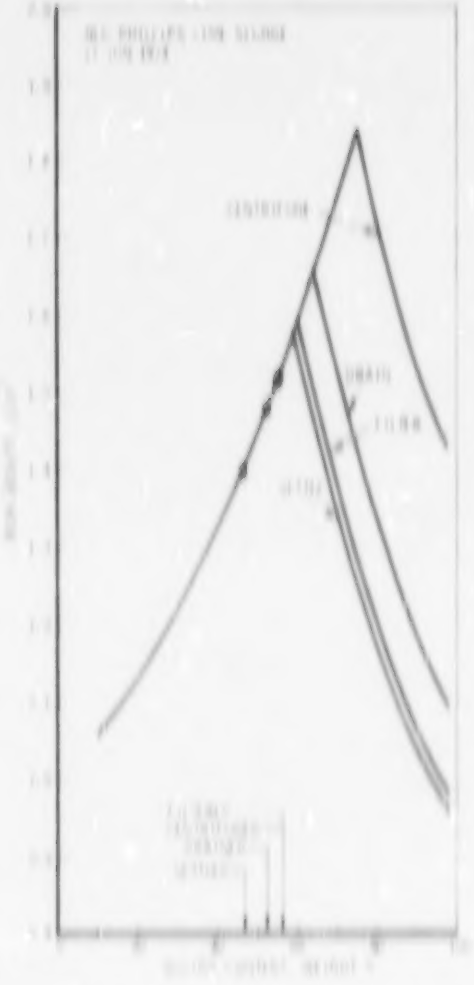

Figure 12. Wet bulk density of DLC Phillips lime sludge and dewatered samples: 17 Jun 1974.

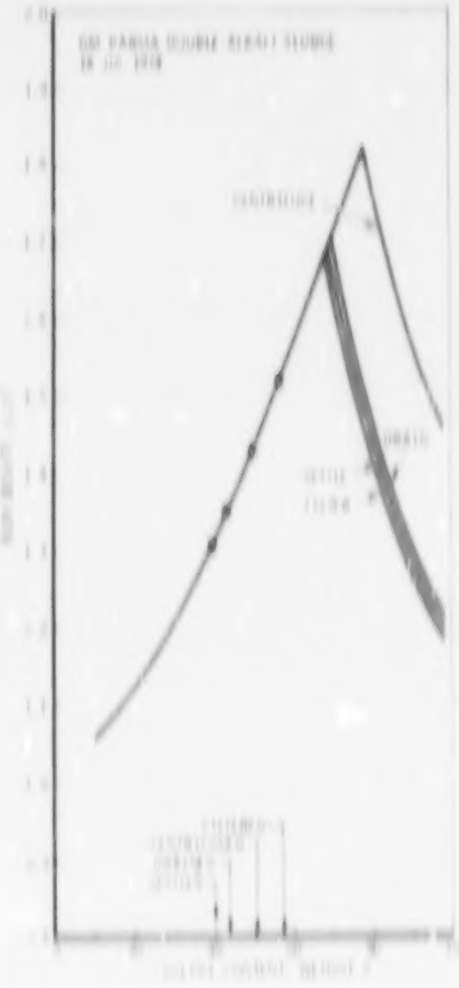

Figure 13. Wet bulk density of GM Parma double-alkali sludge and dewatered samples: 15 Jul 1974.

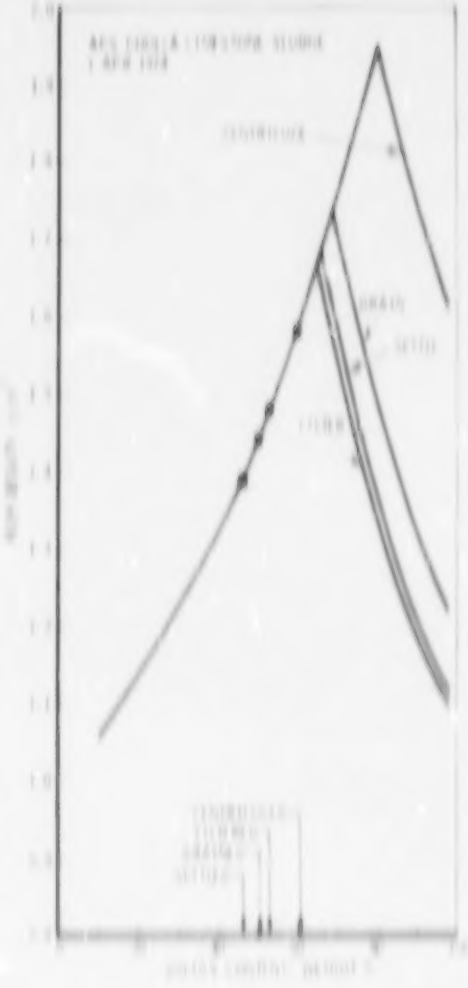

Figure 14. Wet bulk density of APS Cholla limestone sludge and dewatered samples: 1 Apr 1974.

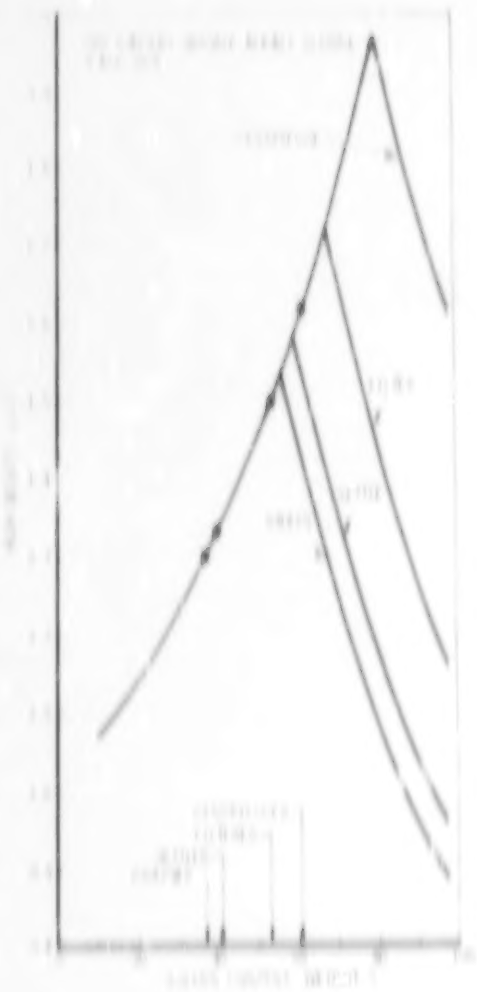

Figure 15. Wet bulk density of UPL Gadsby double-alkali sludge and dewatered samples; 9 Aug 1974.

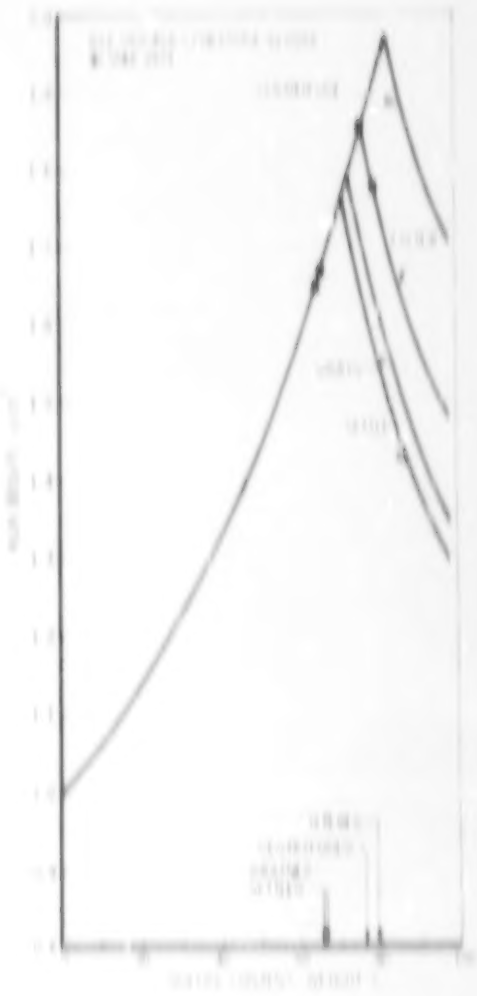

Figure 16. Wet bulk density of SCE Mohave limestone sludge and dewatered samples; 10 Mar 1975.

because the packing of the particle is a function of the forces placed on the particles during the dewatering process.

From the experimental points in Figures 9 through 16, it is revealed that the highest density of sludge is obtained by vacuum-assisted filtration in most sludges and by centrifugation in others. In all cases, relatively small density differences resulted from these two dewatering methods. Moreover, when industrial filters and centrifuges are used rather than laboratory equipment, the difference between the two methods are expected to be indiscernible. In every case, the force of laboratory centrifugation was sufficiently greater than filtration, as revealed by the packing density of particles and by the bulk density of dry sludge (right-hand border of figure), that the expected maximum density obtainable was always greatest by centrifugation. In several sludges, the particle packing obtained by vacuum filtration was not as great as by settling or free drainage even though the actual measured density by filtration was always greater. It is believed that this is because particle packing by vacuum filtration takes place so rapidly that particles do not have the opportunity of assuming minimum volume configurations.

In most sludges, there was little difference in the density of sludges dewatered by settling or by free drainage, nor was there much difference between the expected maximum density as determined by the particle packing density.

A compilation of the dewatering behavior of these sludges is given in Table 10 and includes, for each experimental method, the wet bulk density and solids content, the dry bulk density, the calculated maximum density, and the solids content as given by the intersection of Equations (3) and (4).

These data show that the sludges with the best overall dewatering characteristics, i.e., the TVA Shawnee (limestone), the SCE Mohave (limestone), and DLC Phillips (lime) sludges, were those with the coarsest particle size distributions. The double-alkali systems produced the finest particle size distributions and had the worst dewatering characteristics. The most effective method of dewatering in most cases was by vacuum-assisted filtration. However, centrifugation was nearly as effective and was superior in several instances.

Settling and free drainage did not reveal a significant difference in dewatering characteristics and reflected the similarity of these two methods observed by experimentation. The inference of this observation is that the sludge settles to the same density whether water drains or rises to the surface.

6.5 COEFFICIENT OF PERMEABILITY

The potential pollution capability of sludge liquor is governed by the mobility of leaching waters and is determined by the permeability coefficient of the various media through which these waters must pass. Liquor mobility can be controlled either by (a) containment of the waste in a basin having an impervious liner, (b) chemically treating the waste in such a

TABLE 10. UNTREATED SLUDGE BULK DENSITIES

Sample Source[a]	Settle[b] ρB ρD ρM	Settle[b] %B %D %M	Drain[b] ρB ρD ρM	Drain[b] %B %D %M	Filter[b] ρB ρD ρM	Filter[b] %B %D %M	Centrifuge[b] ρB ρD ρM	Centrifuge[b] %B %D %M
TVA Shawnee Limestone (4/1/73) ρs = 2.48	1.45 1.10 1.65	49.0 100 66.4	1.51 1.09 1.65	55.7 100 65.9	1.63 1.16 1.71	65.0 100 67.5	1.76 1.43 1.86	77.8 100 78.5
TVA Shawnee Limestone (6/15/74) ρs = 2.47	1.40 1.11 1.66	52.3 100 66.8	1.53 1.06 1.64	58.3 100 65.7	1.64 1.15 1.67	65.3 100 68.5	1.60 1.48 1.86	61.3 100 78.1
TVA Shawnee Lime (3/19/74) ρs = 2.53	1.36 0.91 1.54	43.4 100 59.4	1.44 0.97 1.58	41.5 100 60.6	1.51 0.97 1.55	56.0 100 57.1	1.44 1.10 1.73	49.9 100 72.2
GM Parma Double Alkali (12/18/74) ρs = 2.45	1.31 1.20 1.70	49.7 100 69.9	1.32 1.22 1.71	[illegible] 100 71.0	1.52 1.10 1.64	55.8 100 65.1	1.41 1.46 1.84	59.9 100 78.4
UPL Gadsby Double Alkali (8/9/74) ρs = 2.60	1.17 0.90 1.54	41.4 100 59.5	1.30 0.83 1.55	[illegible] 100 [illegible]	1.50 1.16 1.74	58.6 100 67.1	1.62 1.61 1.93	64.2 100 81.2
DLC Phillips Lime (6/17/74) ρs = 2.50	1.30 0.90 1.55	41.6 100 60.9	1.48 1.03 1.65	51.1 100 63.8	1.52 0.98 1.59	57.0 100 62.0	1.54 1.43 1.84	57.2 100 72.1
APS Cholla Limestone (3/17/74) ρs = 2.55	1.51 1.32 1.68	46.7 100 67.1	1.44 1.22 1.77	50.0 100 70.2	1.49 1.10 1.66	57.4 100 64.0	1.58 1.61 1.75	60.9 100 81.4
SCE Mohave Limestone (12/30/73) ρs = 2.55	1.47 1.36 1.56	55.6 100 59.3	1.67 1.35 1.73	67.2 100 71.5	1.50 1.40 1.60	60.1 100 71.2	1.60 1.51 2.11	77.0 100 84.5

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[a] ρs = true density of dry sludge solids (g/cc).

[b] ρB, %B = wet bulk density (g/cc) and solids content (wt %) of unsettled sludge;
ρD, %D = dry bulk density (g/cc) and solids content (wt %) of dry sludge;
ρM, %M = wet bulk density (g/cc) and solids content (wt %) at maximum density.

manner that the waste itself is impermeable, or (c) preventing or minimizing rainwater from recharging the disposal site. Each of these methods of control requires a unique disposal technology and specific attention to disposal management. In the first case, the control by liner containment is independent of the permeability of the waste itself. However, with such phenomena as a breach in the liner as a consequence of earth movement, liner deterioration, or burrowing animals, the control of pollution may then be dependent upon the properties of the waste and soil. Chemically treated waste is expected to produce a material with a lower permeability than untreated waste. In this case, intended control is provided by a reduction in the concentration of chemical constituents that can leach from the treated waste and/or a reduction in the amount of liquid that passes through the waste. In the case of rainwater, control of the amount of liquid passing through the waste is determined primarily as a result of disposal site design and maintenance, and this control can be applied independently of or in conjunction with the other two control methods.

In all three cases, permeability of leaching waters through the waste provides a controlling parameter that serves as a maximum limit to the amount of liquid that recharges the subterranean water supply. The amount of liquid and the level of contamination of this liquid are jointly responsible for the pollution potential of any given waste disposal site. For this reason, the coefficient of permeability of each of the treated and untreated FGD sludges was measured.

6.5.1 Experimental Procedure

The permeability of sludge from seven separate scrubbing facilities was determined by passing deionized water through sludge columns by the constant head technique. Experiments were conducted by packing 100 grams of dried, powdered sludge solids into 4-cm diameter glass columns or 200 grams of dried sludge solids into 6-cm diameter glass columns. The sludges were oven-dried either at 80°C in air or at 70°C in a vacuum until constant weight was achieved. Generally, the finer sludges were dried at the lower temperature, in a vacuum, in order to accelerate the drying process. In all cases, leaching water was added to the column from the top.

The procedure used required a determination of the pore volume by calculating the particle packing density in the column from the weight of the sludge and its height in the packed column. Then a volume of deionized water was added to the column that exceeded the pore volume by nominally 3 percent. The columns were monitored as water slowly worked its way, by gravity, through the packed sludge solids. The excess water was collected in a volumetric cylinder and compared with the calculated excess. In all cases except one, the measured excess and calculated excess were within 1 percent. This was true because all sludges, except one, retained all pore water and, in measuring excess water, it was apparent not only by the absence of supernate water but also because the rate of water dripping from the column abruptly went to zero.

In the evaluation of whether this technique fully wetted the sludge solids, the close correlation between calculated and measured excess water indicates that less than 1 percent unwetted pore space could have remained in any of the columns. Moreover, since the difference between calculated and measured excess water was equally distributed both negatively and positively, it is reasonable to conclude that the difference was a consequence of a random error in measurement rather than a systematic error in pore wetting.

The one exception to this behavior was observed with the SCE Mohave sludge, where more than 2 percent additional excess water was measured over the calculated value. This sludge was also the only one found in the dewatering study that created open pore space by a mechanical dewatering technique. It was further observed that a gradual decrease in the rate of water dripping from the column took place before the rate went to zero. For this sludge, the particle packing density and pore volume were recalculated from measured excess water taken at the point where the drip rate decreased.

The permeation measurements were begun when an amount of deionized water was added to a known height above the top of the sludge; the amount of water percolating through the column was then collected and measured as a function of time.

The procedure just described was also used on chemically treated sludges. Preparation of the samples included crushing and pulverizing the fixed material after drying. The powder was packed into the column in the same manner as the untreated sludge. Although this technique does not provide an accurate value for treated sludge placed in an undisturbed manner, it should provide an upper bound as well as a reasonable description of the permeability of a sludge that is moved after placing and curing.

Additionally, the permeability of undisturbed fixed sludge was determined by the following method. A cylindrical core from a block of fixed material was cut slightly smaller than the inside diameter of the permeation column. A layer of a silicone-based adhesive was applied to the circumferential area of the sample and allowed to cure. A second layer was then applied; the sample was slid into the column; and the adhesive was allowed to cure. Both glass and clear plastic columns were used in order to assure a proper seal between the sample and column wall. In low permeation samples, it was necessary to apply a slight gas overpressure (2 to 6 psig; 4 to 12-ft H_2O) to accelerate the flow of water through the sample.

An additional test procedure was applied to the untreated sludge at the conclusion of the permeation measurement. The supernate water was decanted from the surface of the sludge, and the column was allowed to air-dry for 24 hr. The sludge was then compacted with a plunger, but the thixotropic nature of the material and the high level of retained water did not permit as much compaction as desired. A new column height was measured, and the particle packing density and pore volume were recalculated. The permeation rate was again measured, as previously described.

6.5.2 Permeability Test Results

The results of the permeability tests are presented in Table 11 and in Figure 17. Datum points in the figure are connected by solid or dashed lines representing two different slopes. The lower slope was established by the best fit through the TVA Shawnee limestone permeation data and was applied to the DLC Phillips lime and SCE Mohave limestone data. In all three cases, the same slope adequately represents the results. The steeper slope was selected as the best fit through the TVA Shawnee lime, the APS Cholla limestone, and the GM Parma and UPL Gadsby double-alkali systems. There is no theoretical basis for selection of two slopes rather than individual slopes for each system.

The implication of these data is that permeation through sludge responds in one of two behavior patterns as a function of the amount of compaction of the material. Generally, the sludges that correspond to the lower slope had higher permeation coefficients and compacted to higher particle densities (lower void volume) than the sludges with higher slopes. Moreover, the change in particle density was typically greater for the lower slope sludge, as a consequence of identical compaction conditions.

A probable explanation for the observed behavior may be the difference in particle size between the two groups of sludges. The TVA Shawnee lime system and both double-alkali systems produced a sludge with finer particle sizes than the three sludges showing a low slope and the APS Cholla sludge showing a high slope. If it were not for the Cholla sludge, it might be concluded that the change in slope was solely a function of particle size.

An alternative explanation may be offered that is not intrinsically dependent on particle size but, rather, is a function of the technique of compaction. In all cases, the columns were allowed to air dry for 24 hr. In the coarser particle sizes, the effect of surface tension on the loss of water is less pronounced, and the possibility for greater drying takes place. Therefore, the increase in particle density upon subsequent compaction is a consequence of the sludge being more capable of reaching higher particle density values than the finer particle-sized sludge in which water would not evaporate as readily. Again, the APS Cholla sludge, being coarser in particle size, would be expected to behave as the other coarser particles. However, the Cholla sludge contained a bimodal distribution of particles in which fly ash constituted the finer fraction. It is likely that this distribution, which allowed the finer material to fill the void space between the coarser particles, accounts for the significantly lower permeability of the Cholla sludge at equivalent values of particle density. It may also be that the presence of the finer particles provided the resistance to drying attributed to the finer particle-sized sludges such that, upon compaction, this sludge then behaved like the finer sludges.

Whether either of the mechanisms postulated to explain the observed behavior is correct may be insignificant relative to the observation that the fine-particle sludges reduced permeability coefficients significantly as a result of very small changes in particle density. This behavior may suggest that a more efficient compaction might decrease the permeability

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TABLE 11. PERMEABILITY OF UNTREATED AND CHEMICALLY FIXED FGC SLUDGES

[illegible]	[illegible]	[illegible]	Fractional Void Volume	Permeability [illegible]	Remarks
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Column packed as slurry Compacted set
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Compacted set
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Column packed as slurry
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Compacted set
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Compacted set
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Compacted set
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

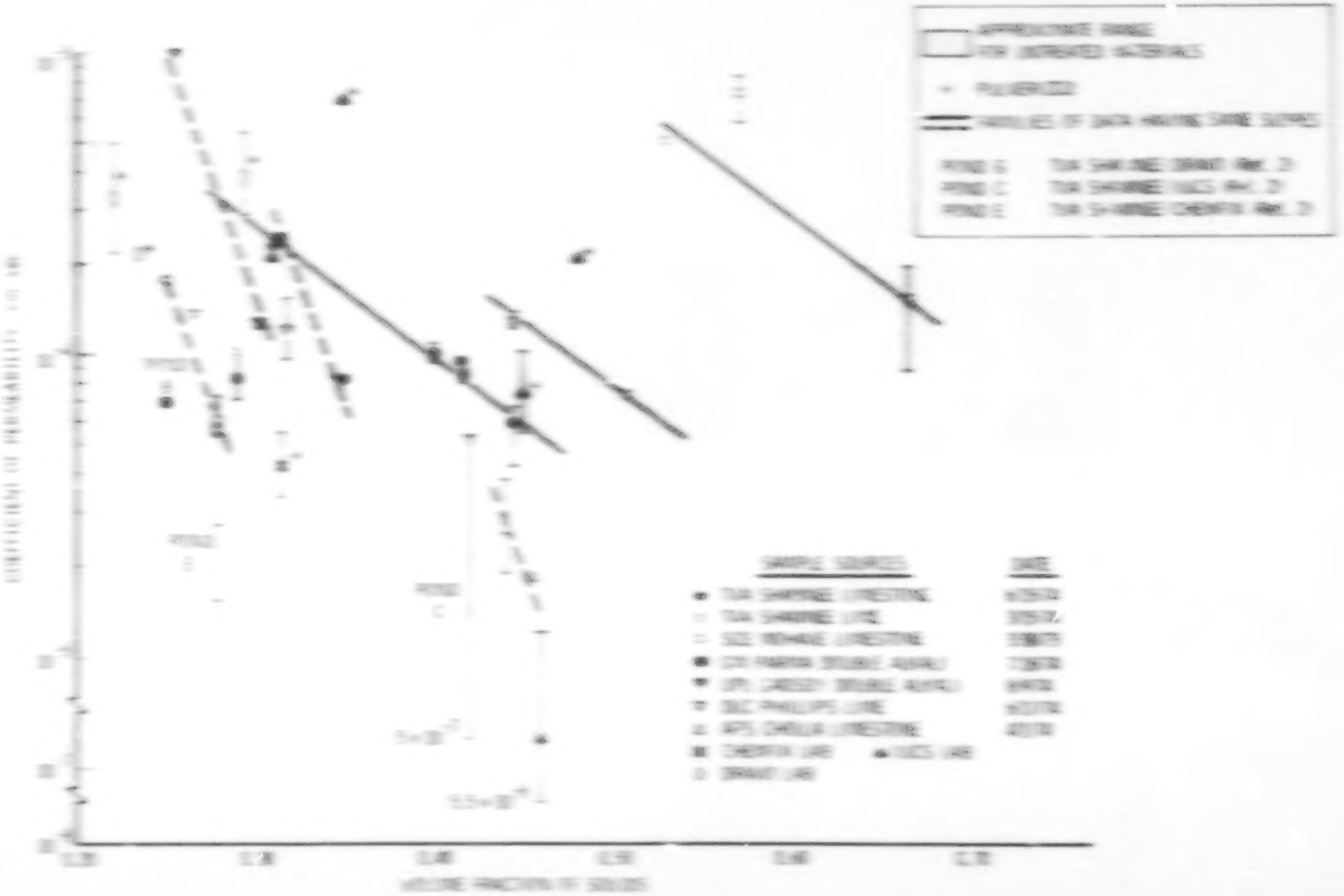

Figure 17. Permeability of treated and untreated sludge: Aerospace analyses.

coefficient even further and, given only a 5 percent reduction in void volume, would produce an order-of-magnitude reduction in permeability coefficients.

On the other hand, the permeability of the compacted sludge may be only a consequence of a spatial redistribution of particles that results in only a small change in particle density. In this case, more efficient compaction may not further improve particle distribution, and the result may be similar to the coarse-particle behavior. Further work is required to clarify this uncertainty.

The data presented in Figure 17 strongly suggest that the permeability coefficient of untreated sludges generally fall in the range of 2×10^{-4} to 5×10^{-5} cm/sec (shaded area of Figure 17) and can be described as typically having a value of 1×10^{-4} cm/sec independent of void volume. This behavior was similarly observed for treated sludges that had been pulverized in the laboratory and which simulated sludges that are moved after placing and curing. The only exception to this general behavior was observed on treated sludges that were not pulverized. In most cases, the permeability was low, similar to concrete materials, and suggests that treated sludges placed and cured without subsequent moving may form a highly impermeable waste basin. Whether all fixation methods will produce similar results is uncertain, but it is reasonable to conclude that the permeability of treated sludge that is placed and not subsequently moved will be less than that of sludge which is moved after placement.

6.6 COMPACTION

One of the considerations in the disposal of FGD sludges is the volume or land area required for placement of the sludge. A previous study (1) has indicated that for pond disposal a placement depth of 30 ft is optimal. Thus, by using a 30-ft thick disposal depth and knowing the rate of sludge production and wet bulk density of the sludge, it is possible to calculate the volume or land area required for disposal. The size of the required land area directly affects the economics of disposal such that the cost of secondary dewatering and mechanical compaction of the sludge enters into the total consideration of sludge disposal technology.

Section 6.4 discusses and compares the results of dewatering techniques; from these data, it is possible to calculate the cost benefits of each method. This section discusses the results of compaction tests conducted on six different FGD sludges relative to the size, shape, and distribution of particles and to the water content of each compaction sample. The compaction tests can be performed only on samples having a moisture content less than the maximum density value defined by Equation (5) and shown in Figures 9 through 16. In this partially dried state, air voids partially fill the free volume between particles, and the function of the compaction process is to rearrange particles in a manner such that these air voids are eliminated. It is erroneous to assume that a maximum density could be obtained at a zero moisture content because the presence of water is necessary to provide lubrication to the particles for facilitation of their motion past each other. The resultant change in sludge density is a consequence of both the available air-void volume and the ability of the particles to slide past each other under the applied load.

6.6.1 Experimental Procedure

The compaction of six FGD sludges was performed by applying a load onto the samples constrained from lateral displacement, recording the change in sample height directly on the loading ram, and comparing the height before and after loading by micrometer measurements. The samples, in all cases, were the dried cake from the wet bulk density study that had been dewatered by settling in a free draining condition. From each sludge cake three disks were hand-carved, 1.25-in. in diameter and nominally 0.05-in. in height, such that they fit snugly into a pellet die. The dry disks were placed in a humidity chamber for various periods of time and were withdrawn when they reached a selected moisture content based on dewatered sludge properties shown in the bulk density curves in 6.4.2. These were stored individually in sealed plastic containers where they were allowed to equilibrate for one week before being tested.

The tests were conducted by first weighing the samples to determine the precise moisture content, measuring the sample height, and carefully inserting the sample into the pellet die. The plungers were inserted into the die and placed into a constant strain test machine, and a 125-lb load (≈ 100 psi) was applied. From the displacement of the ram on the test machine and from the height of the sample after being withdrawn from the pellet die, volume changes were calculated.

6.6.2 Compaction Test Results

The stress-strain behavior of the sludges during the compaction tests are presented in Figures 18 through 23. The solids content was selected at three nominal values (79, 86, and 93 percent levels), representing three levels of air-dried sludge. As shown, it is apparent that the amount of water in the samples had a marked effect on the compaction that occurred under load. In general, the most compaction took place at the highest moisture content, and the least compaction took place at the lowest moisture content. However, several exceptions to this generality are noted, specifically in the APS Cholla sludge. The compaction of the sludge under maximum load ranged from 15.5 percent for the TVA Shawnee limestone sludge down to slightly over 2 percent for the DLC Phillips sludge. Except for the TVA Shawnee sludges, maximum compaction was generally only 5 to 7 percent.

When the compacted sludges were removed from the die and measured with a micrometer, the sample heights were all found to be greater than the heights indicated on the testing machine. The percent volume change by compaction calculated from these heights is indicated in the figures by arrows. These results indicate that upon removal of the die wall constraints, the samples returned to nearly their original height. In other words, these

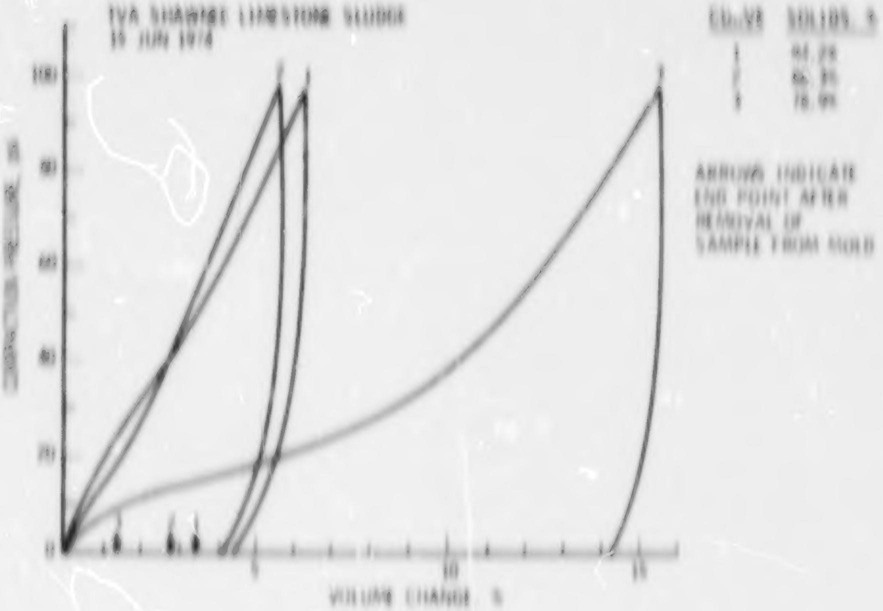

Figure 18. Compaction test results for TVA Shawnee limestone sludge solids.

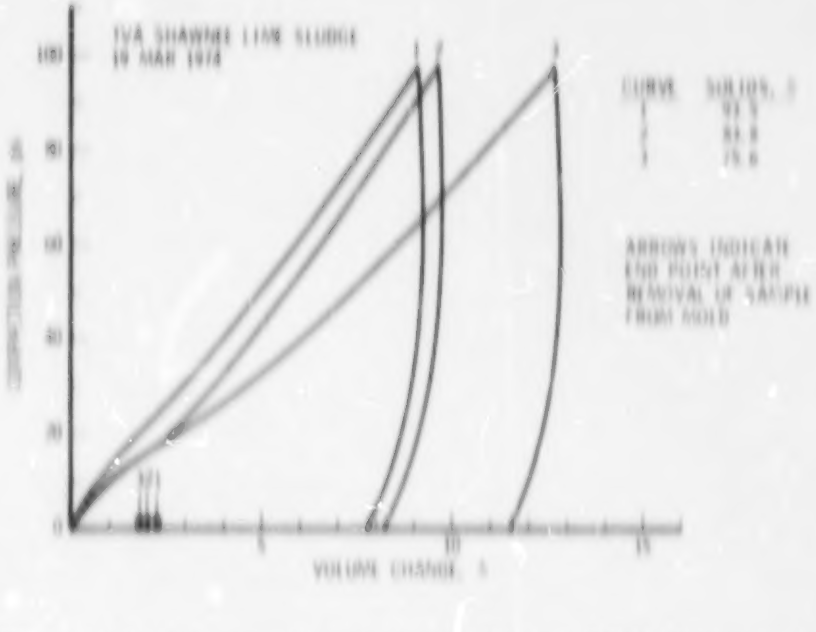

Figure 17. Compaction test results for TVA Shawnee lime sludge solids.

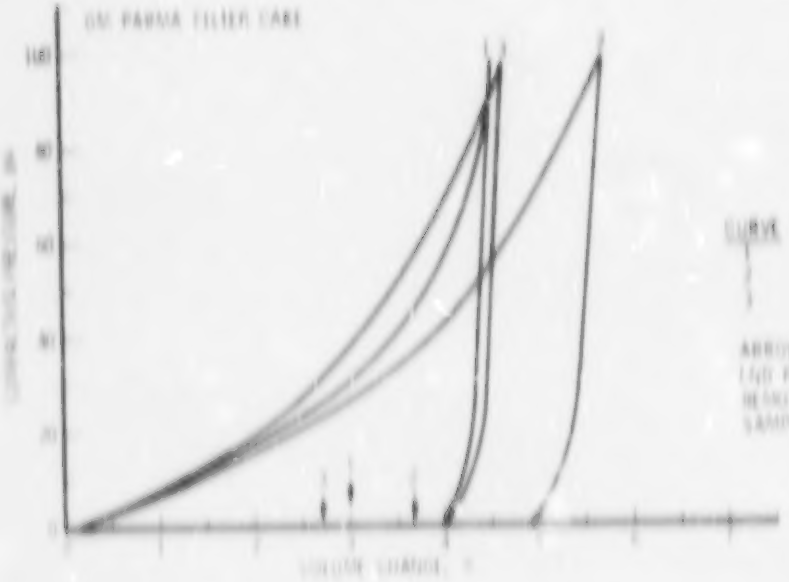

Figure 20. Compaction test results for GM Parma filter cake solids.

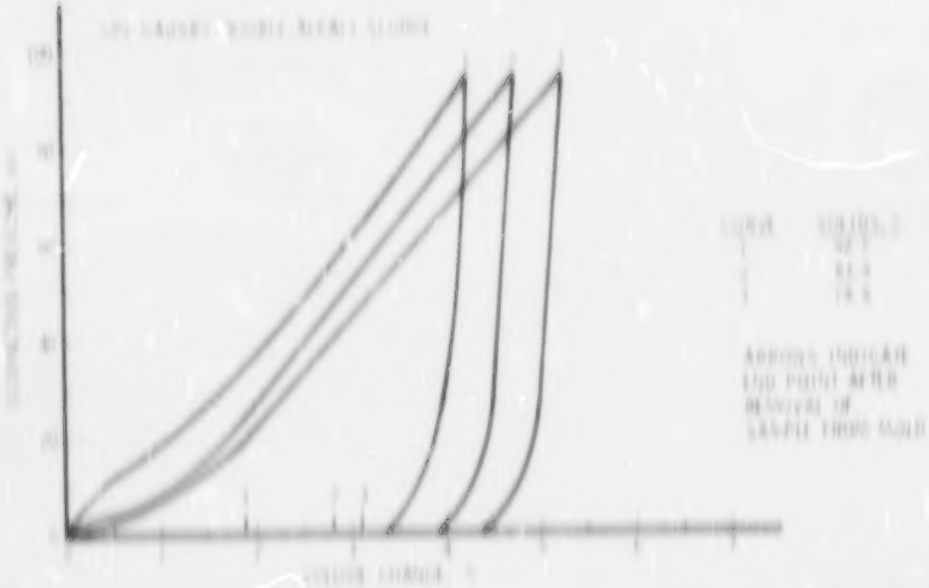

Figure 21. Compaction test results for UPL Gadsby double-alkali sludge solids.

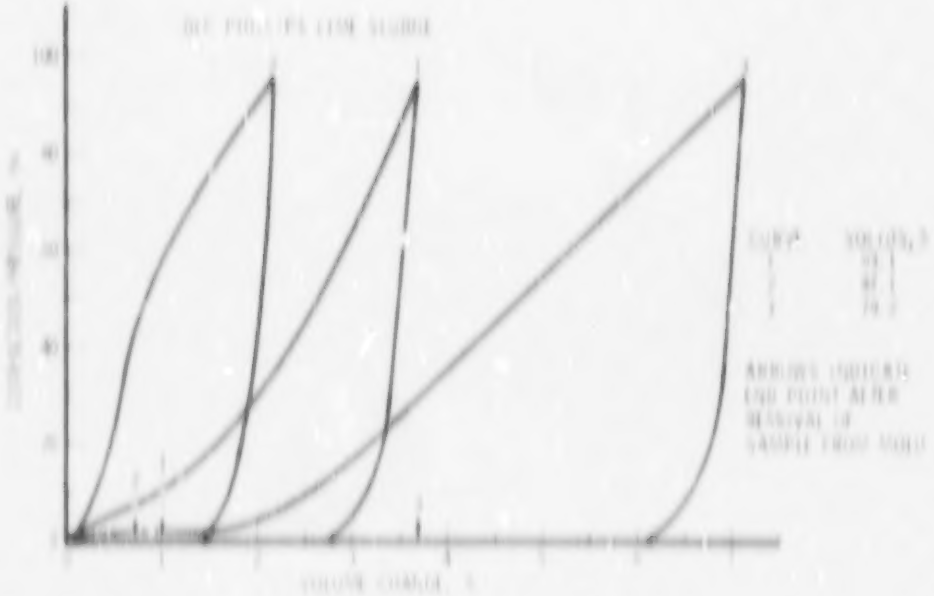

Figure 22. Compaction test results for DLC Phillips lime sludge solids.

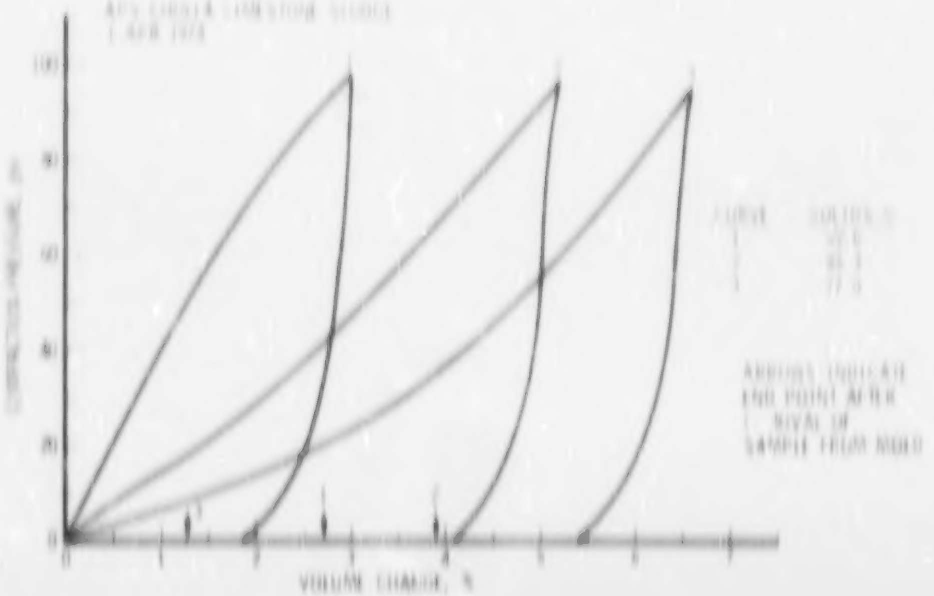

Figure 23. Compaction test results for APS Cholla limestone sludge solids.

results indicate that the compaction observed in the test was nearly all elastic compaction and little repacking of particles under load occurred. The permanent deformation that was experienced was as small as 1 percent and did not exceed 4 percent in any of the sludges.

The wet bulk density at each value of solids content, when normalized to a dry bulk density basis, is an indication of the permanent change in particle packing. These values are plotted in Figure 24 and show that little compaction takes place. For contrast, a compaction envelope taken from seven different fly ashes compacted and sampled in the field (15) was plotted. For fly ash, minimum compaction was about 7 percent, and maximum compaction was nearly 20 percent. Thus, the results experienced from compacting fly ash are not to be expected in field sludge compaction on the basis of these data.

An explanation of this behavior is to be found in the crystalline morphology of the sludges. For sludges having platy calcium sulfite crystals, it is easy to envision that particles packed together bend and deflect when stress is applied such that the particles again return to their original configuration when the stress is removed. For lath-like gypsum crystals, the growth trend is to form intergrown crystals, with the result being a loosely packed, open network of crystals; in some cases, the presence of fly ash in the sludge will fill the interstices between the crystals. Force applied to this arrangement of particles flexes the gypsum crystals and possibly breaks the intergrown clusters, but increased particle packing is difficult. Only in those cases where particles are reasonably blocky does effective packing take place, and this took place only in the GM Parma and APS Cholla samples, among the six sludges tested.

The consequence of limited permanent deformation is that an increase in strength and decrease in permeability coefficient expected from compaction is not realized. Because particle rearrangement is evidently not affected by compaction, strength is not measurably increased. However, the small permanent deformation that is experienced is sufficient to reduce water passage, and the permeability of the compacted material is reduced by a factor of two (Section 6.5).

6.7 COMPRESSION

The compression test is used as a general measure of the strength of FGD material and is judged by comparison with soil material. The value of this test is to provide a relative measure of the strength of a material in a simple and straightforward manner. It is not useful as an engineering test because it does not account for the strengthening effect of contiguous material in landfill placement. The lateral constraints afforded by adjacent material can produce strengths that are greater, by 3 to 5 times, than the strength of freestanding material.

For FGD waste disposal in landfill applications, a comparison of soils and sludge provides an effective means for evaluating the acceptability of waste in the useful reclamation of a waste disposal area. Moreover, the

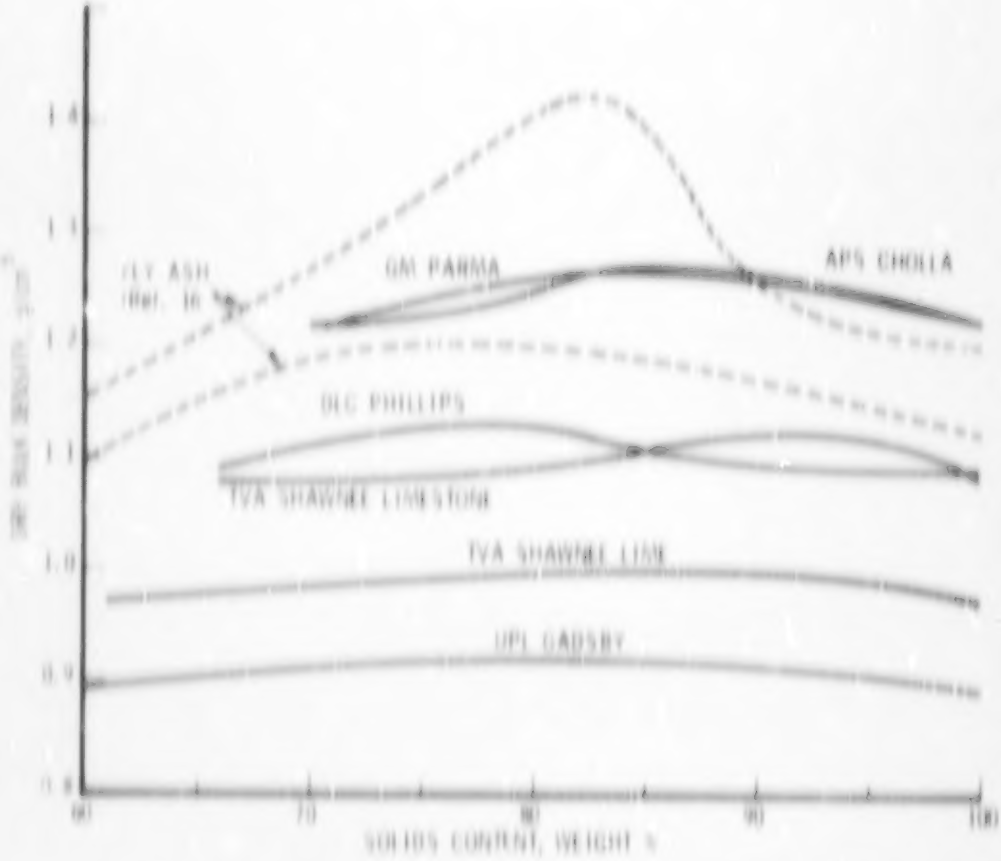

Figure 24. Compaction of FGD sludge (dry basis).

additional strength provided by chemical treatment processes can be evaluated for potential structural fill applications.

6.7.1 Experimental Procedure

Compression strength tests were conducted essentially in accordance with the standard test methods (18) defined by ASTM C 39-64. Test samples of untreated FGD wastes were prepared by casting slurries of the waste material into containers nominally 2 in. in diameter and 4 in. in length. Excess water was removed by decanting from the surface and through weep holes in the base of the mold. Samples of chemically treated FGD wastes were tested either as supplied by the manufacturer or as cut and machined by conventional machining tools.

Samples were tested under two conditions, in a full dry state and in a state of about 10 percent moisture (or at the moisture content as received in the case of treated sludge). Drying of samples was by air, accelerated by the heat from the upper surface of a conventional laboratory drying oven.

6.7.2 Compression Test Results

The results from the compression tests of dried untreated sludges were generally unsatisfactory because of the inherent difficulties in preparing samples. The major problem with untreated materials was caused by cracking during drying and was possibly a consequence of large shrinkage in some cases. In other cases, samples chipped or crumbled during the simple handling procedures required to prepare flat, parallel loading surfaces. Because of the generally difficult preparation, samples were accepted for testing that are not acceptable by normal standard test method procedures. Whereas three samples were cast for each representation of a single sample of sludge, only in one case was it possible to test all three. In several cases, no samples were available for testing; in other cases, one or two samples were tested, but the samples were not all acceptable because of dimensional defects.

The results of compression tests are given in Table 12 where the strength of each sample is recorded as a function of moisture content within the sample. In many cases, the strength of the samples as measured was lower than that which would be expected if the sample had not experienced dimensional defects. In other cases, very low strength is suspected as a consequence of incipient shrinkable cracks.

The test results show that untreated sludge is not readily compared with soil (1.5 to 7 tons/ft^2). The difficulty in preparing samples for testing is generally indicative of the problems expected on the surfaces of air-dried sludges in the field. Air-drying, possibly assisted by solar heating, will produce a material that shrinks and cracks such that when loaded the material will crumble.

The chemically treated laboratory samples had strengths that indicated more than adequate stability for structural fill purposes. Values are

TABLE 12. UNCONFINED COMPRESSION TEST RESULTS

Sample Source	Moisture Content, %	Strength, kg/cm²	Remarks
	Oven Dried Samples[a]		
TVA Shawnee Limestone (2/1/74)	8.9	1.6	--
	0.0	0.6	Shrinkage cracks
TVA Shawnee Limestone (6/15/74)	7.4	2.4	Chipped edge
	10.1	1.4	--
	0.0	0.8	Loading surface chipped
	0.0	1.1	Cracks on surface
	0.0	1.3	Cracks on surface
TVA Shawnee Lime (3/19/74)	14.4	0.9	--
DLC Phillips Lime (6/11/74)	5.9	2.0	--
	8.7	2.1	--
	10.4	1.7	--
	0.0	1.2	Slight shrinkage cracks
	0.0	[illegible]	Slight shrinkage cracks
	0.0	1.4	Slight shrinkage cracks
GM Parma Double Alkali (7/18/74)	--	--	No samples retained integrity
APS Cholla Limestone (4/1/74)	5.6	1.4	All samples retained shape and edges
	7.2	1.5	
	8.1	1.6	
	0.0	1.7	
	0.0	1.5	
CEI Gadsby Double Alkali (8/7/74)	--	--	All samples cracked
TVA Shawnee Limestone (Chemfix)	--	--	Material in granular form
TVA Shawnee Limestone (IUCS)	1.2	46.7	Samples prepared in IUCS laboratory
	2.4	48.5	
	0.0	52.1	
DLC Phillips Lime (Calcilox)	5.6	25.4	Material fixed by DLC, using Calcilox additive at the Phillips station
	9.2	22.1	
	Cured in Field Samples[a]		
TVA Shawnee Limestone (Chemfix)	31	2.4 to 5.6	Analyses of core samples taken from the EPA Shawnee Field Disposal Evaluation Project (Ref. 2)
TVA Shawnee Limestone (Dravo)	38	1.9 to 2.4	
TVA Shawnee Limestone (IUCS)	31	19.3 to 31.7	

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[a] Oven dried samples had strengths that were 6 to 48 percent higher than those of the cured in field samples.

also given in Table 12 for samples that were obtained from the TVA Shawnee field evaluation project (2) and analyzed in the as-cured condition. These provide confirmation that chemically treated sludges attain adequate structural strength.

SECTION VII

CHEMICAL CHARACTERIZATION OF UNTREATED FGD WASTE

The environmentally acceptable techniques for ultimate disposal of FGD wastes are those that do not permit excessive quantities of chemical pollutants to enter the environment. The sources of chemical pollutants are the process ingredients consisting of combustion products of coal, lime or limestone absorbents, and process makeup water. Soda ash is a potential pollutant source in the double-alkali system. For this study, chemical pollutants are defined as those elemental or compound species that, if allowed to enter the environment, may be detrimental to the health or well being of man, animals, or natural plant life for reasons of their toxic, or otherwise undesirable, nature. Trace elements found in coal and limestone include heavy metal elements that are known to have a toxic effect on living organisms when their concentration exceeds an acceptable tolerance limit. In addition, major chemical species involved in the scrubbing process, although not hazardous to man, can nevertheless be a noxious irritant if allowed to enter the environment in an uncontrolled manner. The objective of the task reported in this section is to characterize flue gas desulfurization (FGD) sludges and the process ingredients from which they originate so as to provide an understanding of the relationship between the source and fate of potential chemical pollutants within the various FGD scrubbing processes.

7.1 OVERVIEW AND ASSESSMENT

Chemical analyses of FGD waste were performed for differing scrubbing facilities under various operating conditions and design parameters. The evaluation of these data clearly reveals that the concentrations of trace elements found in sludge solids are directly dependent upon the concentrations of those metals found in the input ingredients, primarily the combustion products (fly ash) of coal. The concentrations of these elements in sludge liquors are shown to be similarly dependent upon their content in the coal and are presumed to result from the leaching of fly ash.

As a consequence of the direct relationship between trace element content in sludge and in coal, it is expected that trace elements originating in coal will be found principally in the sludge. When comparing eastern and western sludges, it was found that western sludges had concentrations slightly less than eastern sludges, particularly for arsenic, cadmium, mercury, and zinc, which are found in significantly lower concentrations in western coal.

When the chemistry of the scrubbing liquor is investigated as a function of scrubber absorbent, i.e., limestone, lime, or double alkali, it is found that, in general, the trace element content in the liquor is highest in the limestone systems, intermediate in the lime systems, and lowest in the double-alkali systems. The most probable systematic parameter that affects these differences is the pH of the scrubber liquor. The limestone scrubbing systems operate at the lowest pH, and the double-alkali systems operate at the highest pH. When a limestone and a lime system both operating on the same coal (TVA Shawnee facilities) or two systems operating at equivalently high sulfate concentrations and ionic strengths (SCE Mohave and GM Parma) are compared on a one-to-one basis, the same relationship between scrubber pH and trace metal content is found. This relationship suggests the role of pH in the leaching of fly ash.

An evaluation was made of the trace metal content in the system liquor at various stages in the disposal process from the scrubber to the final disposal site. The analyses indicated that the pH of the system liquors increased and trace element concentrations metals showed a decrease enroute through the system. These results may be interpreted as a response to system pH or a response to the changes taking place in the concentration of major chemical species. The in-process analyses revealed a rapid oxidation of sulfite ion and a precipitation of calcium sulfate. The trace metal content in the liquor may have decreased by precipitation in response to decreasing ionic strength, by co-precipitation resulting from the scavenging action of the calcium sulfate, by adsorption onto newly created surfaces of the calcium sulfate phase, or by pH changes.

However, when the chemical analyses of trace elements in all liquor samples from every power plant sampled are evaluated as a function of pH or of ionic strength, no correlation is apparent. It was determined from these data that changes in ionic strength do not affect the measured concentration of trace metals and that pH changes affect these concentrations only within a system where major system parameters are invariant. From the positive correlation of liquor analyses with coal combustion product analyses, it is shown that trace metal content in system liquor is primarily controlled by the content of these metals in the coal and only secondarily controlled by the pH of the system. Moreover, the pH control can be seen only when coal, the primary controlling parameter, is invariant as observed in in-process changes or when comparing the processes which use the same coal source, e.g., the TVA Shawnee facilities.

When the chemical species in system liquor are evaluated over a period of time, the data indicate that all species increase from startup. The calcium sulfate saturation level is established quickly as is the concentration of trace metals. Chloride ion concentrations appear to build up at a slower rate and continue to build up until a steady state is established. As the chloride ion concentration increases, a concomitant increase in ionic strength causes higher calcium sulfate saturation levels. Trace element contents in the liquor do not reflect these changes, and this result is consistent with the previous observation of invariance with changes in ionic strength, indicating that trace metals are not saturated in system liquors and concentrations are primarily dependent on the coal content (through fly ash) and on the removal from the system of these elements through occluded liquor in the sludge.

This section presents a brief description of the power plant scrubbing facilities that provided the data base for this report; descriptions of the sampling procedure and subsequent chemical analyses; and a discussion of the various relationships that were observed between scrubber chemistry and the many variables of the scrubbing process and process ingredients. Comparisons and contrasts of the various scrubber designs, eastern and western coal, and lime and limestone absorbents are given, and the role of fly ash in the trace element content of FGD sludges is identified.

7.2 POWER PLANT SCRUBBING FACILITIES, SAMPLING, AND CHEMICAL ANALYSES

The data base for this study was generated from samples taken from the power plant scrubbing systems listed in Table 13. A complete chemical characterization of the scrubbing process was performed on six of these systems, and a more limited analysis was performed on the remaining system. These FGD systems represent full-scale units having greater than 100-MW equivalent generating capacity, as well as prototype and pilot-scale systems of only 1-MW equivalence of generating capacity. Lime, limestone, and double-alkali systems are represented, as are both eastern and western coals. For the purpose of this study, the effect of these system design variables was investigated relative to the scrubber waste chemistry and the potential of these wastes as an environmental pollutant source.

Appendix B describes each scrubbing facility from which samples were obtained. Periodic samples were obtained from many of these facilities, and the specific conditions existing for each sampling are described. In addition, a schematic diagram of the scrubbing facilities is presented, with an identification of the sample source locations.

7.3 CHEMICAL ANALYSES

7.3.1 Experimental Procedure

As a general procedure, samples were taken by the scrubber system operating personnel. Some samples were filtered at the site to arrest reactions between liquor and solid reagents. All samples were packaged in containers and shipped to The Aerospace Corporation.

Upon receipt of these samples at the laboratory, all slurry samples were filtered through Whatman No. 40 filter paper, and the pH and sulfite content of the filtrate were determined at once. Liquid samples were

TABLE 13. FLUE GAS DESULFURIZATION SYSTEMS SAMPLED AS DATA BASE

Power Plant	Scrubber System	Scrubbing Capacity, MW (equiv)	Coal Source	Absorbent
Tennessee Valley Authority (TVA) Shawnee Steam Plant	Venturi and spray tower, prototype	10	Eastern	Lime
TVA Shawnee Steam Plant	Turbulent contact absorber, prototype	10	Eastern	Limestone
Arizona Public Service (APS) Company, Cholla Power Plant	Flooded-disc scrubber, wetted film absorber	120	Western	Limestone; fly ash
Duquesne Light Company (DLC), Phillips Power Station	Single- and dual-stage venturi	110	Eastern	Lime
General Motors (GM) Corporation, Chevrolet-Parma Power Plant	Bubble-cap tower	32	Eastern	Soda ash; lime
Southern California Edison (SCE) Mohave Generating Station	Turbulent contact absorber, pilot plant	~1	Western	Limestone
Utah Power and Light (UPL) Company, Gadsby Station	Venturi and mobile bed, pilot plant	<1	Western	Soda ash; lime

stored in small polyethylene bottles and frozen. Solids samples were dried at 70°C and stored in sealed polyethylene storage bags.

All chemical analyses were performed by standard chemical analysis techniques, in accordance with, at the very least, the minimum criteria identified by the EPA Analytical Quality Control Laboratory (19-21). A description of the chemical analysis methods are presented in detail in Appendix C for both liquids and solids. In every case, both the accuracy and precision of the method were determined with respect to analyses of the scrubber liquors.

The results of the chemical analyses are presented in tabular form in Appendix D; slurry analyses are given in separated form, i.e., liquid and solid. The effluents identified as "separated" are those samples which were filtered at the sampling site. Samples identified as "retained" are those that are filtered at Aerospace, as were those not identified.

7.3.2 Results of Chemical Analyses

The results of the chemical analyses from the sources presented in Appendix D are summarized in Table 14. The range of chemical constituents were taken from the analyses of the sludge samples after the final stage of dewatering, when leaving to enter the disposal basin.

Several observations can be made from these data that reveal the chemical constituent concentrations that may be expected from FGD scrubber systems. Among the trace elements in sludge liquors, the higher range of concentrations were generally less than 1 mg/ℓ with only three exceptions, aluminum, arsenic, and selenium; none of these were significantly greater than 1 mg/ℓ. The highest values for all others lay between 0.1 and 1 mg/ℓ except for mercury, which had a maximum value of 0.07 mg/ℓ. In nearly each case, the total range of liquor concentration for any element lay within two orders of magnitude. This trend appears similar to the concentration for trace elements in the solids, except that the magnitude of the concentrations were generally greater by a factor of 100 relative to the liquor.

A correlation exists between the liquor and solids concentrations of beryllium, cadmium, and mercury, in that the values were generally lower in both phases, which appears to indicate that these elements were in the sludges in relatively minor amounts. On the other hand, concentrations in the solids were generally high for chromium and zinc (possibly, also, copper), but these higher values were not reflected in the range of liquor concentrations. Whereas in the first case the correlation strongly suggests a concentration limitation based on input amounts, in the second case, the lack of correlation more nearly suggests that solubility may have been controlling the liquor concentrations of these elements. An apparent exception to these correlations was selenium, which had the broadest concentration range in the liquor (nearly four orders of magnitude) but had the narrowest concentration range in the solid (factor of eight).

TABLE 14. RANGE OF CONCENTRATIONS OF CHEMICAL CONSTITUENTS IN FGD SLUDGES

Scrubber Constituent	Sludge Concentration Range[a]			
	Liquor, mg/l (except pH)[b]		Solid, ppm[c]	
Aluminum	0.03	- 2.0	-	-
Arsenic	<0.004	- 1.8	0.6	- 52
Beryllium	<0.002	- 0.18	0.05	- 6
Cadmium	0.004	- 0.11	0.08	- 4
Calcium	180	- 2600	105,000	- 268,000
Chromium	0.015	- 0.5	10	- 250
Copper	<0.002	- 0.56	8	- 76
Lead	0.01	- 0.52	0.23	- 21
Magnesium	4.0	- 2750	-	-
Mercury	0.0004	- 0.07	0.001	- 5
Potassium	5.9	- 100	-	-
Selenium	<0.0006	- 2.7	2	- 17
Sodium	10.0	- 29,000	-	- (4.8)
Zinc	0.01	- 0.59	45	430
Chloride	420	- 33,000	-	- (0.9)
Fluoride	0.6	- 58	-	-
Sulfate	600	- 35,000	35,000	- 473,000
Sulfite	0.9	- 3500	1600	- 302,000
Chemical Oxygen Demand	<1	- 390	-	-
Total Dissolved Solids	2800	- 92,500	-	-
pH	4.3	- 12.7	-	-

[a] Data derived from Appendix D

[b] Liquor analyses were conducted on 13 samples from 7 power plants burning eastern or western coal and using lime, limestone, or double-alkali absorbents.

[c] Solids analyses were conducted on 6 samples from 6 power plants burning eastern or western and using lime, limestone, or double alkali.

Among the major species, the concentrations of sulfate and calcium are dependent upon the solubility of gypsum. When relatively high values of sodium or chloride are present, they result principally from additions of either absorbent or makeup water. As the major FGD waste, sulfur can exist either in the sulfate or sulfite phase. As may be expected, the solids sample having the highest sulfite content also had the lowest sulfate content.

One of the most important parameters in the liquid portion of the sludge is the total dissolved solids (TDS). By the nature of the chemical reactions that take place in the scrubber, the value for TDS can be expected to be reasonably high. For the lime and limestone systems, TDS generally approximates 10,000 mg/ℓ. Higher values were observed in the double-alkali sample and in a sample in which salt was added to the makeup water. Lower values were observed in two systems during startup and in a third system operating in a partial open-loop operation.

7.3.3 Determination of Material and Ionic Charge Balance

To ascertain whether liquor analyses are complete and internally consistent, determinations of material and charge balances are of considerable importance. Material balance is obtained by comparison of the sum of the ion concentrations with the concentration of TDS. A deficiency of the former relative to the latter may be indicative of the presence in the liquor of soluble species for which analyses have not been conducted. However, because of limitations concerning the accuracy of analyses, discrepancies may exist between the results of these measurements for individual samples. Examination of the results of measurements for a number of similar samples is often necessary to determine whether true deficits exist. If the sum of the ion concentrations is significantly greater than the TDS, it is almost certain that an analytical error has occurred.

An independent test is obtained by comparison of the sum of the (equivalent) concentrations of positive ions (cations) with the sum of the (equivalent) concentrations of negative ions (anions). Imbalances of ionic charge alone do not unequivocally indicate where the analytical results are in error. In conjunction with TDS data, the charge balance data are much more useful. The signs of the imbalances help to pinpoint the discrepancy. For example, if there is a TDS surplus and an excess of negative ionic charge, there must be a deficit among the cation analyses. Similarly, with a TDS deficit and an excess of positive ionic charge, one or more of the cation analyses must be too high. If the ionic charge is in balance and there is a material imbalance, the TDS measurement is probably in error.

Material balances and charge balances have been computed from analyses of 40 samples of sludge liquor, and the results are shown in Tables 15 and 16. Only two liquor samples were excluded from the available data because analyses had not been conducted for several components. The results have been grouped according to source and date of sampling for comparison of average imbalances. Six sources are represented, four of which were sampled from two to four times each. For each sampling date, from

TABLE 15. MATERIAL BALANCE

Sample Source[a]	No. of TDS Surpluses	No. of TDS Deficits	Average Net TDS Surplus (or Deficit), %	Average Absolute TDS Imbalance, %
TVA Shawnee Limestone (2/1/73)	1	1	− 1.0 ± 2.8	2.0 ± 1.4
TVA Shawnee Limestone (7/12/73)	2	0	2.3 ± 2.9	—
TVA Shawnee Limestone (11/27/73)	2	0	31.0 ± 34.9	—
TVA Shawnee Limestone (6/15/74)	0	4	− 3.1 ± 2.5	—
SCE Mohave Limestone (3/30/73)	3	0	15.6 ± 1.2	—
TVA Shawnee Lime (3/15/74)	4	1	3.0 ± 4.8	4.8 ± 3.5
TVA Shawnee Lime (5/16/74)	2	3	2.8 ± 4.4	4.1 ± 2.7
TVA Shawnee Lime (6/27/74)	4	0	5.2 ± 1.9	—
APS Cholla Limestone (4/1/74)	3	0	4.2 ± 1.2	—
APS Cholla Limestone (11/7/74)	2	0	7.3 ± 6.3	—
DLC Phillips Lime (10/4/73)	3	1	1.6 ± 4.0	2.9 ± 2.2
DLC Phillips Lime (6/17/74)	3	0	3.8 ± 2.5	—
GM Parma Double Alkali (7/19/74)	3	0	7.6 ± 5.3	—
All Samples	32	10	4.9 ± 9.9	7.2 ± 8.5

[a] Results of TDS measurements may be high for one or more samples.

TABLE 16. IONIC CHARGE BALANCE

Sample Source	No. of Cation Deficits	No. of Anion Deficits	Average Net Cation (or Anion) Deficit, %	Average Absolute Ion Imbalance, %	Comments
TVA Shawnee Limestone (2/1/73)	1	1	4.1 ± 11.5	8.2 ± 5.7	a
TVA Shawnee Limestone (7/12/73)	2	0	20.5 ± 4.4	—	—
TVA Shawnee Limestone (11/27/73)	0	2	− 0.9 ± 0.3	—	—
TVA Shawnee Limestone (6/15/74)	4	0	9.5 ± 4.2	—	—
SCE Mohave Limestone (9/30/73)	0	3	− 1.7 ± 0.6	—	—
TVA Shawnee Lime (3/19/74)	5	0	16.8 ± 9.9	—	b,c
TVA Shawnee Lime (7/26/74)	4	1	3.0 ± 5.0	4.7 ± 3.0	
TVA Shawnee Lime (6/27/74)	0	4	− 8.8 ± 8.0	—	—
APS Cholla Limestone (4/1/74)	1	2	− 2.0 ± 4.3	3.7 ± 3.6	—
APS Cholla Limestone (11/7/74)	2	0	41.3 ± 17.6	—	a,c,d
DLC Phillips Lime (10/4/73)	1	1	− 3.9 ± 6.6	4.7 ± 5.5	—
DLC Phillips Lime (6/17/74)	3	0	29.7 ± 5.9	—	e
GM/Parma Double Alkali (7/18/74)	0	3	−12.0 ± 5.4	—	
All Samples	23	17	6.4 ± 15.3	11.7 ± 11.9	—

[a] Results of chloride analyses may be high for one or more samples.

[b] Results of sulfate analyses may be high for one or more samples.

[c] Results of calcium analyses may be low for one or more samples.

[d] Results of sodium analyses may be low for one or more samples.

[e] Results of magnesium analyses not included.

two to five samples are included. In Table 15, the average net TDS surplus or deficit is given, together with the corresponding standard deviation. Average absolute (disregarding sign) TDS imbalances are also given, together with the standard deviation where both surpluses and deficits occurred within a sample group. For all 40 samples, the average net TDS surplus was 4.9 percent with a standard deviation of 9.9. The corresponding average absolute TDS imbalance for all 40 samples was 7.0 percent with a standard deviation of 8.5. Only 2 of the 13 groups showed net TDS deficits, although 10 of the 40 individual samples showed deficits, for a ratio of TDS surpluses to deficits of 3:1. For one group of two samples, with an average TDS imbalance of 31 percent, TDS measurement errors are indicated, as shown in the comments column of Table 15, since the ionic charge was in balance for both samples. For one group of samples, the measured TDS ranged from 92,000 to 95,000 mg/ℓ. Since the analyses give, at most, three significant figures, the observed imbalances of 14 to 17 percent for the three samples of this group constitute better agreement than justified by the accuracies of the data. Only for 1 sample, of the remaining 35 samples, was the TDS imbalance greater than 10 percent. Therefore, it may be concluded, tentatively, that no major soluble species has been overlooked in the analyses.

The results of ionic charge balance calculations are shown in Table 16. For the 40 samples, the average absolute ion imbalance was 11.7 percent with a standard deviation of 11.9. There were 23 samples with cation deficits (anion surpluses) and 17 samples with anion deficits (cation surpluses). The average net cation deficit (anion surplus) for all samples was 6.4 percent with a standard deviation of 15.3. Seven groups showed average net cation deficits, and six groups showed average net anion deficits. Thus, no systematic analytical errors are likely. Nine of the 40 samples showed charge imbalances greater than 20 percent. These nine samples were members of the five groups with average absolute imbalances greater than 10 percent.

The results of analyses of each of these nine samples were examined and compared with the results for other samples within the same groups or other groups representing the same source sampled at different dates. On this basis, each of the imbalances greater than 20 percent can be attributed to one or more of six explanations shown in the "Comments" column of Table 16.

Additional analyses for magnesium and repetition of questionable analyses to complete the listed corrections have not been possible, principally because of the depletion of sample supplies. However, it may be concluded from the results which have been given that satisfactory ionic charge balances have been obtained for 85 percent of the liquor samples that were analyzed. Together with the satisfactory material balances shown for 90 percent of the samples analyzed, the results of the charge balance calculations demonstrate an excellent validation of the analytical data which have been reported.

7.4 EFFECT OF SCRUBBING PROCESS VARIABLES ON SCRUBBER LIQUORS

The effects of scrubbing process variables on the chemistry of the scrubber system was determined by evaluation of the results of the chemical analyses presented in Section 7.3. The variables that were investigated are (a) in-process variations in the scrubber liquor composition as the liquor leaves the scrubber (or scrubber recirculation loop) to the point of discharge from the system; (b) variation in composition of system liquor as a function of time, as determined from periodic sampling; (c) effects of liquor pH or ionic strength on the liquor composition; (d) effect of differences in chemistry of limestone, lime, and double-alkali scrubber systems on the trace element content of sludge liquors; (e) influence of the trace element content in coal on the trace element content in the sludge; (f) effect of coal source (i.e., eastern or western) on the trace element content in the sludge; and (g) relationship between the trace element content in fly ash and the trace element content in the sludge.

The discussion in the following subsections are based on the chemical analyses performed on specific samples. In most cases, the explanations offered are believed to be generally applicable to all like systems. However, it is recognized that these data are limited and interpretation of these data could change in the light of a larger data base.

7.4.1 In-Process Variations in Scrubber Liquor Composition

An evaluation was made of the changes that take place in the process stream of scrubber liquors, from the scrubber effluent to the final filtering or dewatering. The questions to be answered are as follows:

a. What chemical constituents undergo systematic variations, increases or decreases, in the scrubber liquor system circuit?

b. Do in-process variations depend on the scrubber system involved (limestone, lime, or double-alkali)?

c. To what mechanism may changes be ascribed (synergistic change, coprecipitation, or solution of constituents from fly ash)?

Data were compiled for all major, minor, and trace constituent analyses for five scrubber systems, in the form of graphs (presented in Appendix E) showing the concentration of each constituent, from the scrubber through intermediate process steps to the final filtration or clarifying operation. Figure E-1 in Appendix E presents data for the TVA Shawnee (turbulent contact absorber (TCA) and venturi systems, and for the GM, Parma; the DLC Phillips, and the SCE Mohave systems. The APS Cholla scrubber system was not included in this analysis, as it is actually a parallel, two-stage process, and further sampling would have been required to characterize either stage.

TABLE 17. NET CHANGE IN SCRUBBER LIQUOR COMPOSITION OF MAJOR, MINOR, AND TRACE CONSTITUENTS BETWEEN INITIAL AND FINAL STAGES IN SCRUBBER SYSTEM

From the graphic array of data in Appendix E, Table 17 was prepared, showing the overall increases or decreases in each constituent passing through the circuit. It is useful to define how the chemistry of solutions is expected to affect each element or chemical species in the scrubber liquor. These fall into four groups:

a. Metals which are at least moderately soluble in the scrubber circuit, defining this term to include the alkaline earths calcium and mercury, despite the relatively low solubilities of their sulfate and carbonate compounds. The alkali metals potassium and sodium are in this category.

b. The greater number of heavy metals, including the transition metals, which form insoluble oxides, hydroxides, and sometimes carbonates. These are most likely to respond to changes in pH, becoming less soluble as pH increases.

c. A few metalloids, arsenic, boron, selenium, and silicon, which form weakly acidic oxides and at high pH, soluble sodium salts. At low pH, only silicon oxide is highly insoluble; the others, arsenic, boron, and selenium would not be pH sensitive.

d. The anions chloride, fluorine, sulfate, and sulfite whose salts are generally soluble but, except for chloride, form insoluble calcium compounds. A few trace metals (silver, molybdenum, and mercury) form insoluble chlorides, but their quantity is insufficient to reduce the chloride level substantially. Conversely, the presence of these anions might affect certain cations; for example, a high SO_4 level may reduce the lead content by formation of $PbSO_4$.

The following discussion presents on an element-by-element basis the patterns of depletion or enrichment that occurred for each scrubber system.

Aluminum

A uniform decrease in aluminum occurred; this correlated with a rising pH and indicates the precipitation of $Al(OH)_3$. Aluminum actually reaches its minimum solubility at a pH of about 6.0 and at a higher pH may be slowly redissolved by hydrolysis. This effect may be present in the TVA Shawnee lime process samples for 16 May 1974, which showed an initial decrease in aluminum content, followed by a smaller increase.

Arsenic

Arsenic showed an increase in one sample set from the limestone series and a decrease in four sample sets from both the lime and limestone systems, with four sets remaining unchanged (within 20 percent). The arsenic in the GM Parma double-alkali system, which operates at a high pH, was below the detection limit of 0.004 ppm, even though arsenic at 14 ppm was substantial in the GM Parma coal. It is likely that a good deal of As_2O_3 escaped from the stack, and the amount that dissolved in the scrubber underwent little change in concentration.

Antimony

Antimony showed a decrease in one sample each of the lime and limestone series and no change in two other sample sets from the lime systems. Noted decreases were small and indicates a slight tendency toward removal in the system.

Beryllium

In the lime and limestone systems, no sample set showed an increase; two showed small decreases; and seven remained unchanged. Thus, the overall process underwent no significant change in beryllium. The beryllium content of the double-alkali system was below detection (<0.005) although the coal content, 1 ppm, was the highest in beryllium of those analyzed. This may reflect precipitation of the oxide at high pH, although no pH effect could be discerned for the lime and limestone systems.

Boron

Boron decreased in the lime system, but this was not a response to a change in pH. It may be evidence of the removal of an insoluble calcium borate.

Cadmium

Cadmium showed no pattern of changes for the limestone system samples, but in the lime system samples, there were two decreases in cadmium and two with no change. This is attributable to the precipitation of the insoluble hydroxide, $Cd(OH)_2$, with increasing pH. The fact that it did not take place at all times may indicate the importance of removal processes, i.e., coprecipitation and scavenging.

Calcium

There was a general pattern of decrease in the calcium content for the lime and limestone systems and a slight rise in calcium for the double-alkali system. The decrease was in accordance with the slow growth of crystals of insoluble calcium salts to the size where separation occurs. It was not paralleled, however, by a decrease in sulfate content and can not be fully explained without reference to the role of bisulfite in controlling the calcium content.

Chromium

There were two increases in chromium content in the limestone system samples, one decrease, and two with no change. In lime system samples, the proportions were one increase and two with no change; in the double-alkali system, the chromium content was below detection (<0.02 ppm). This element, then, showed no evidence of a systematic in-process change in any of the three systems.

Cobalt

There was a decrease in the cobalt content of the only sample set representing the limestone system. The lime system samples showed an increase in cobalt in one sample set, with a second sample set remaining at the same level. It is possible that, for the limestone system, the in-process addition of a limestone slurry depressed the cobalt level by formation of the insoluble $CoCO_3$.

Copper

There was no general change in the copper content for any of the three systems.

Iron

Iron decreased in the single analysis of a limestone system sample set and in three lime system sample sets. Forming an insoluble hydroxide, it would be expected to show a decrease with the downstream increase in pH.

Lead

For the limestone system, two sample sets showed an increase in lead content and two showed a decrease. The lime system samples showed no change in the lead content in four sets; consequently lead was considered unchanged. For the double-alkali system, there was an increase in the level of lead, although it would seem that, in promoting the formation of the basic carbonate, the addition of lime and soda ash would have had the opposite effect. There is no apparent explanation for this increase in lead unless it is introduced in the lime or soda ash.

Magnesium

Analyses of magnesium were run for four limestone system sample sets, and three lime sets; no appreciable change was observed in any of these.

Manganese

Analyses of manganese were made for two lime system sample sets; one of them showed an increase and the other a decrease in manganese content. Overall, the manganese was considered unchanged.

Mercury

Two decreases in Hg were noted for the limestone system, three unchanged values for the lime system, and one decrease for the double-alkali system. The pattern, therefore, is one of a uniform decrease in mercury content. This element forms insoluble oxides, carbonates, and chlorides, all of which may have contributed to purging it from the liquor.

Nickel

Nickel likewise decreased for the limestone and one lime system sample set. A second lime system set showed no change in nickel, but the net effect was a decrease. This is accountable as a function of pH, representing removal of insoluble nickelous oxide. The carbonate was also insoluble, as was a basic carbonate, $2\ NiCO_3 \cdot 3\ Ni(OH)_2$, which would have formed at a higher pH.

Potassium

Changes in potassium were the same for all three systems, i.e., a low to moderate increase to levels no greater than 20 percent except for the double-alkali system clarifier No. 2 underflow. This increase is believed to represent the slow dissolution of potassium from silicates present in the fly ash carried over into the scrubber and, possibly, as a contaminant in the soda ash of the double-alkali system.

Selenium

Selenium in four limestone system sample sets showed two increases and two unchanged. The levels, for four lime system sample sets, showed one decrease and three unchanged. One selenium sample set in the double-alkali system decreased about 50 percent as it passed through the No. 1 clarifier.

Silicon

Three lime system analyses showed a reduction in silicon content, but only one of these was substantial (about 33 percent); the others were slight. The decrease was predicted on the use of the scrubber-effluent-retained sample at 4-ppm silicon, as the initial point. The scrubber-effluent-separated sample was only 2-ppm silicon; the difference is believed to be silicon that was dissolved from fly ash in the period of approximately two weeks after the sample was taken. Therefore, it is likely that in the scrubber circuit itself there was no real change in silicon content for this system.

Silver

Silver decreased in one limestone and two lime system sample sets and showed no change in a third lime system set. This may be construed as a net decrease ascribable to removal of insoluble chloride, oxide, or carbonate of silver with increasing pH.

Sodium

There was no change in sodium in two sample sets; one a limestone process and the other a lime process set. A third lime process sample set showed a loss of 50 percent of the sodium content of the in-process liquor. This is considered unaccountable.

The double-alkali system, to which sodium was added in the form of carbonate in midprocess, was not included in this evaluation because its value in the final waste is dependent upon the efficacy of the filter cake washing operation.

Zinc

In the limestone system sample sets, the zinc increased slightly in one instance, decreased in three, and remained the same in another. Likewise for the lime system, it decreased in three sample sets, the net effect being a decrease in zinc. It may represent the precipitation of a zinc carbonate, $ZnCO_3$. For one sample set in the double-alkali system, there was an increase in zinc content as it passed through the No. 1 clarifier.

Chloride

A decrease in Cl^- occurred for all four sample sets for the TVA Shawnee limestone system. There is no obvious mechanism for this decline in a readily soluble ionic species, but it is noted that Cl^- forms many weak complexes with metals, including calcium, and these may be scavenged from solution by fly ash, by precipitating calcium salts or by unconsumed calcium sulfite, $CaCO_3$. The lime systems showed only two small decreases in chloride, with two sample sets remaining unchanged; evidently the chloride removal process is much less effective in this system. Finally, the double-alkali process indicated an in-process gain in chloride. This might result from the introduction of small amounts of NaCl with the soda ash. On the other hand, the systems trend from a decrease to an increase paralleled the level of pH of the systems. For an alternative explanation, the concentration of chloride may decrease as these ions or complexes are adsorbed on surfaces of newly forming precipitates as in the limestone process, but at a higher system pH the hydroxyl ion competes for these sites with no net gain or loss as in the lime process. However, in the double-alkali system, the increase in circuit pH may favor the adsorption of the hydroxyl ion sufficiently that chloride ions or complexes are desorbed, for an increase of chloride in the system liquor.

Fluoride

In the limestone system, the fluoride content showed an increase for the two sample sets analyzed, presumably due to the slow solution of the fluoride present in the fly ash. The lime and double-alkali systems showed no change in chloride content, probably because the higher pH of these systems is less effective in leaching fluoride from the fly ash.

Sulfite and Sulfate

In all cases, sulfite oxidized rapidly downstream of the scrubber, and the resultant sulfate either increased to saturation or remained at saturation levels (see Section 8.3.1).

Total Dissolved Solids

The in-process TDS content would be expected to parallel those of its major constituents, calcium chloride and sulfate, and this was, in fact, the case. TDS in the limestone systems showed decreases in all sample sets. The lime system had two sample sets showing a decrease in TDS and one other remaining unchanged. TDS in the double-alkali samples showed a considerable in-process increase between the mixing Tank No. 2 underflow and the filter effluent, correlating closely with the sulfate content.

pH (Hydrogen Ion Concentration)

Since the overall scrubber process is one of neutralization of a sulfurous acid liquor, the pH is expected to rise from scrubber to filter. It did so for all eight sample sets of the limestone and lime systems. For the double-alkali system, the initial upstream point is at the No. 2 Mixing Tank, after the addition of the neutralizing lime. Consequently, no further change in pH may be traced in the circuit.

From the graphic presentation of data in Table 17, overall increases or decreases of constituents can be observed. Summing up all changes in concentration, it is noted that there were 27 increases, 72 decreases, and 78 without significant change (<20%). On an element-by-element basis, it appears that only potassium and fluoride showed a general increase in concentration; that aluminum, boron, calcium, iron, mercury, nickel, silicon, silver, chloride, sulfate, and sulfite showed a decrease; and that the remainder were unchanged or responded in a manner too subtle to be clearly discernible as they passed through the process circuit. In all cases (except the double-alkali process), the TDS decreased and the system pH increased from the scrubber to the point of disposal.

On the whole, the scrubber bleed system is one in which many elements appear to be removed by coprecipitation or scavenging, probably by the formation and growth of sulfite or sulfate because of the rapid oxidation of the bisulfite ion. Also, most of the remaining constituents are unchanged in concentration as they pass through the circuit. Except for the increases in potassium and fluoride, both attributed to leaching of fly ash, the concentration of major, minor, and trace elements in the scrubber liquors tends to decrease along the process circuit.

System dependence is apparent for magnesium for the limestone and lime process, possibly because of the competing mechanisms involving dissolution and precipitation as a function of pH change in the process. Chloride ion content is seen as a system variant for all three scrubbing systems, possibly also a consequence of absorption or coprecipitation. The changes in calcium, sodium, and sulfate concentration in the double-alkali systems are attributed to intentional in-process chemistry. However, selenium and zinc decreased and increased, respectively, in the double-alkali system for which no clearly understood mechanism is apparent.

7.4.2 Variation in Composition of Sludge Liquors with Time

It is predictable that during the startup period of a scrubber system, an increase in dissolved solids takes place. Thereafter, if the liquid circuit is completely closed-loop, there would be a slow increase in the more soluble constituents such as salts of sodium and magnesium, while the less soluble ones, including salts of most of the trace elements, would level off at their saturation values. If the circuit is not entirely closed, allowing some solubles to escape in the pond slurry or filter cake, soluble constituents in the recirculating liquors would reach steady state levels determined by the bleedoff rate. Thus, to determine whether constituents of sludge liquors undergo any significant changes in concentration during extended periods of operating time, plots were made (Appendix E, Figure E-2) of the major and trace constituent levels in the disposal liquor of each set of samples as a function of sampling date. The scrubbing systems selected for this evaluation were those for which multiple sample sets had been analyzed over time periods ranging from 4 to 16 months. These plants were the TVA Shawnee TCA process, the Shawnee venturi process, the DLC Phillips venturi process, and the APS Cholla venturi absorption tower process.

Sample series included a set taken shortly after startup from the TVA Shawnee lime process and one from the TVA Shawnee limestone process. For the lime process, the first sample was taken on the third day after startup, and an interval of about two months elapsed between the initial sampling and the second sampling. During this period, the concentration of 15 constituents including all major species increased in the liquors; the concentration of 3 trace constituents decreased; and the concentration of 5 trace constituents remained practically unchanged. There was a general buildup of ionic species between the first and second sampling shown in a 50 percent increase in TDS.

A third sample set was taken approximately two months after the second sample set. The TDS increased an additional 15 percent, reflecting the increasing concentration of all the major chemical species, but the number of trace constituents that increased totaled 10 compared to 9 trace constituents that showed a decrease and 3 trace constituents that showed no change in concentration. Moreover, of the 10 trace elements that showed an increase between the second and third sampling, only 5 of these showed an increase between the first and second sampling. Thus, among the trace species, only lead, potassium, sodium, silicon, and fluoride ions showed a consistent increase over the four-month period, whereas all major chemical species increased significantly during this time.

The other scrubber system sampled in the startup period, the TVA Shawnee limestone process, was first sampled about six weeks after an intermittent period of operation in an open-loop mode. The second sample was taken approximately five months later. In this time period, all the major chemical species showed an increase in concentration, reflecting an increase in TDS of 300 percent. Among the trace species, seven increased; five showed no appreciable change; and none showed a decrease. A third sample was taken after 10 months from the initial sample. The TDS increased an insignificant amount reflecting chemical stability during this time period. However, in this time period eight trace constituents decreased; one remained virtually unchanged; and only two trace constituents increased, chromium and copper, both continuing their increase from the initial sampling.

The fourth sampling was taken about six months later at a point in the TVA Shawnee experimental program when large quantities of magnesium were introduced into the scrubber loop. The result was a significant increase in TDS, primarily as a consequence of soluble magnesium sulfate. All trace metals decreased in this period, except beryllium and lead. This latter sampling may not be appropriate for consideration in this evaluation because of the large increase in sulfate ion concentration.

The DLC Phillips station was sampled twice, about eight months apart. All of the trace elements analyzed in both sets of samples either showed a decrease or were virtually unchanged. The TDS dropped sharply during this period as a consequence of operation in a more open-loop mode. The trace elements would be expected to decrease for the same reason.

The APS Cholla station was sampled twice about seven months apart. In this time period, the TDS increased more than 50 percent primarily as a consequence of chloride buildup. During this time, nine trace elements increased in concentration; five decreased; and four were unchanged.

For the four power plants evaluated, it has been observed that from startup there is a rapid buildup in the concentration of major species that can reach relatively stable conditions at a concentration where the rate of constituent loss in the solid waste product is exactly equal to the rate at which that constituent is scrubbed from the flue gas. Among the trace elements, with the exception of lead, it is deduced from these data that after a buildup period during startup there are no systematic time-related trends in concentration levels for the trace constituents of the liquor. Small trends, of course, may have occurred for a few elements, notwithstanding the generally inconclusive data. The fact that trace element concentrations do not change systematically with time nor with changes in major species concentration indicates that they are controlled by some factor other than saturation chemistry.

The variation in concentration of a given element from one set of samples to the next is ascribed principally (lead possibly being an exception) to the effects of differences in input (coal content) to operating conditions, and in the case of low-concentration-level trace metals to low analytical precision. It should be noted that in the case where TDS increased because of an increase in sulfate content, the trace elements decreased, but when the TDS increase was caused by chloride ion increase, the trace elements increased. This behavior suggests that sulfate ion may be exercising some chemical control on the content of trace elements. Insufficient data are available to provide confirmation of this observation.

The relation of trace element concentrations of sludge liquors with scrubber operating time, when measured in terms of several months, is summarized as follows:

a. Trace element concentrations are not time-dependent, barring an initial startup period.

b. Fluctuations in concentration are ascribed principally to variations in trace element content of process ingredients (fuel, reactant, and process water) and operating conditions.

7.4.3 Effect of pH and Ionic Strength on Concentration

The evaluation of the chemical analyses presented in Sections 7.4.1 and 7.4.2 revealed a general decrease in trace element content as pH increased. In Section 7.4.2, it was observed that TDS (and therefore ionic strength) increased with the time of scrubber operation. No correlation could be detected for trace elements, except possibly for the case of lead. On the basis of these observations, correlations between trace element concentrations, pH, and ionic strength were attempted to determine whether more precise correlations of these parameters with the concentrations of trace elements could be determined.

A plot of the concentrations of eight trace elements as a function of system liquor pH is presented in Appendix E, Figure E-3. It is expected that if hydroxyl ion concentration were controlling the trace element concentrations, a maximum concentration of the trace element would be reached at each value of pH as a decreasing function with increasing values of pH. No indication of direct pH control of the trace chemical species can be detected from these data (see Section 8).

A plot of the solute concentration of trace elements as a function of the ionic strength of the system liquors is presented in Appendix E, Figure E-4. In this case, it would be expected that the maximum concentration of a trace element would increase as ionic strength increased. Again, no correlation could be established.

In most scrubber systems, pH is used as a system control. In Figure 25, ionic strength is plotted as a function of pH. The purpose was to determine whether the hydroxyl ion concentration is influential in controlling the concentration of major species. (The double-alkali systems were not included in these analyses.) As before, no correlation is apparent from these data.

The conclusion that must be drawn from the data, presented in Appendix E, Figure E-3 and E-4, is that trace element concentrations within the scrubber liquors are not controlled by either system pH or the ionic strength of the liquor. This conclusion is in agreement with the results, discussed previously, which ascribe trace element concentrations in system liquors to the variations in trace element content of process ingredients and to major system design variables as demonstrated in Section 8. It is not apparent in any of these analyses that a level of saturation had been reached by any of the trace elements.

7.4.4 Comparison of Selected Solute Trace Elements in Sludge Liquors from Limestone, Lime, and Double-Alkali Scrubber Systems

Overall concentration levels of solute trace elements in scrubber liquors using the limestone, lime, and double-alkali processes were evaluated to determine whether levels differed appreciably for the three processes.

A graphic representation of the variation among specific scrubber systems, showing median values for individual systems, is presented in Figure 26. For example, the bar for arsenic-limestone shows the range of median values of arsenic within each of the three scrubber systems: APS Cholla, SCE Mohave, and TVA Shawnee, using the limestone process.

The graph shows that in most cases there is considerable overlap in range of trace element levels between power plants using different scrubbing processes and different sources of coal. Comparing the lime and limestone systems in Figure 26 for six elements shows that the range for the lime system lies within the range for the limestone system; for three elements, the range for the lime system lies below, but overlaps, the range for the limestone system.

Comparing the single set of double-alkali system samples (GM Parma) to the lime and limestone systems shows that for at least one element the double-alkali system lies below the range for the limestone systems and, for one other element, the double-alkali system lies above the range for the lime and limestone systems. For all other elements, the concentration lies always less than midway within the range for the lime and limestone system.

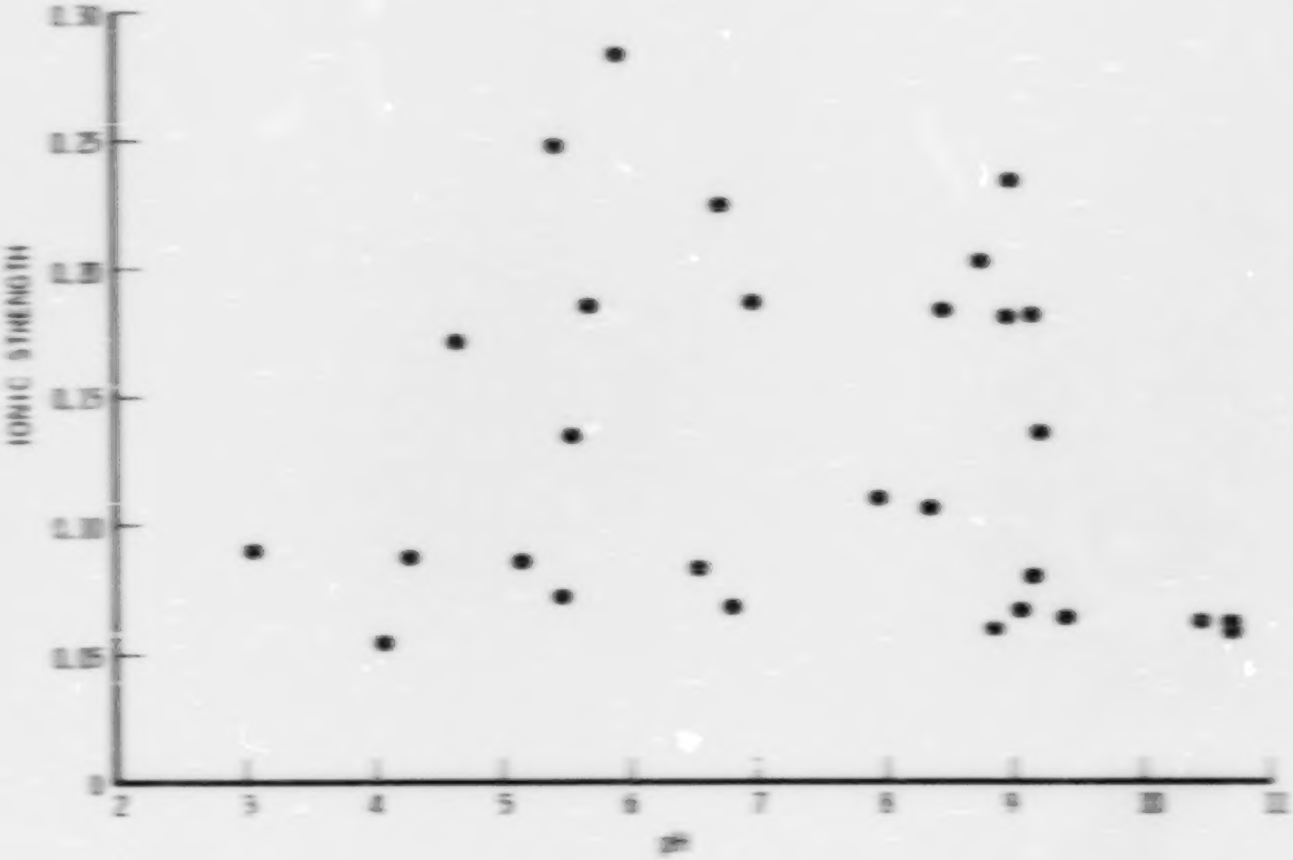

Figure 25. Relationship between liquor system pH and ionic strength.

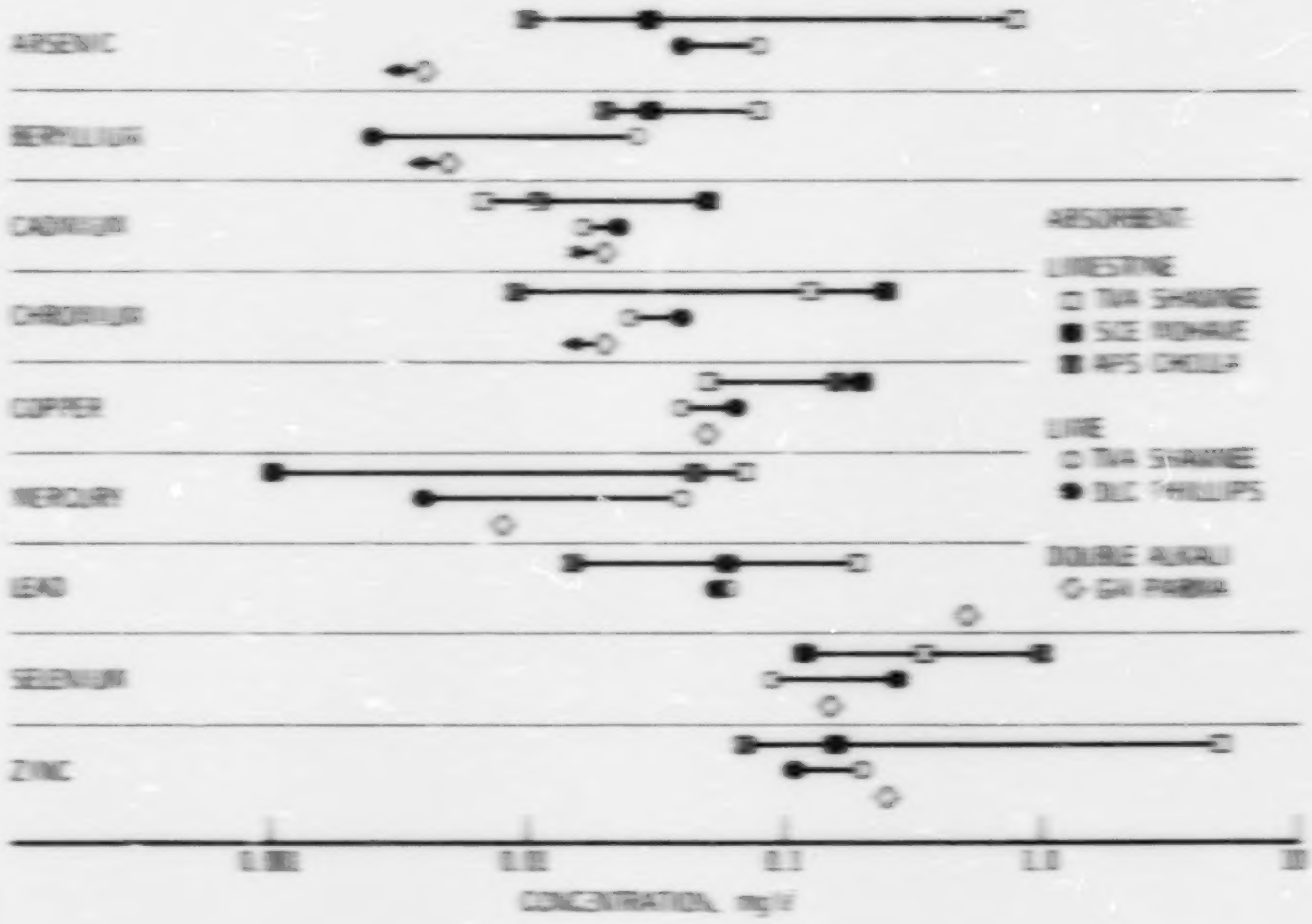

Figure 26. Median values for trace element concentrations in sludge liquors of three absorbent systems.

If a direct comparison of individual facilities is made, other observations are possible. Comparing the GM Parma and SCE Mohave systems, both operate with electrostatic precipitators (resulting in low levels of fly ash in the sludge) and comparably high ionic strengths. The concentrations of five trace elements are clearly greater in the SCE Mohave liquor, and for two trace elements the concentrations are clearly greater in the GM Parma liquor. For two other trace elements, the difference in concentrations is not discernible. In a comparison of the TVA Shawnee limestone and Shawnee lime, for all but one trace element the limestone liquor has higher concentrations than the lime liquor, but for at least two of these trace elements the difference is not great.

The effect of system absorbent is summarized in Table 18, which shows that, in nearly every case, the trace metals were highest in the limestone system, intermediate in the lime system, and lowest in the double-alkali system. The only obvious system parameter that can account for this order of trace metals is scrubber pH, which was lowest in the limestone systems and highest in the double-alkali system.

TABLE 18. RELATIVE PROPORTIONS OF TRACE ELEMENTS IN LIMESTONE, LIME, AND DOUBLE-ALKALI SLUDGES

Element	Scrubber System		
	Limestone	Lime	Double Alkali
As	High	Medium	Low
Be	High	Medium	Low
Cd	Medium	High	Low
Cr	High	Medium	Low
Cu	High	Low	Medium
Hg	High	Medium	Low
Pb	Low	Medium	High
Se	High	Medium	Low
Zn	High	Low	Medium

These specific comparisons support the general observation that suggests that scrubber pH has an effect on the solute trace metal content but that system pH is not generally influential. In the specific comparisons of the two TVA Shawnee facilities, the predominantly higher trace concentrations in the limestone system is particularly significant because less makeup water is used in that specific lime system.

These comparisons show that while, in general, the trace metal levels in limestone systems were high and those in the double-alkali system were low, the variance among individual scrubbing facilities was as great as or greater than the variance among different systems. Through the comparisons of scrubbing systems, there is support for the conclusion that the determining factors in trace metal levels in liquors are primarily system variables that control the input, principally the amount entering the system, and the output that leaves the system as water. System chemistry, in particular scrubber pH, has a recognizable influence, but the effect of other system variables, such as residence time and percent solids in the sludge in circuit and system efficiency as determined by mechanical design, may contribute to the establishment of the solute trace metal concentration level.

7.4.5 Relationship of Trace Element Content Between Input Ingredients and Scrubber Sludge

In previous subsections, it has been suggested that process input ingredients, i.e., coal, alkaline absorbent, and makeup water, may directly affect the concentration of trace metals in the scrubber sludge. In this subsection, the comparison is made of the trace element content in process ingredients and in the solid and liquid portion of scrubber sludges originating from these materials. In determining the content of trace metals in process ingredients, the contribution of the absorbent and process water was determined by adding to the coal a value based on the stoichiometric ratio of the absorbent to the sulfur content of the coal. In all cases, the contribution made by process waters was found to be insignificant relative to the contribution made from coal, and the correction due to the absorbent, in most cases, modified the coal analysis only slightly. A graphical representation of these comparisons are made for sludge solids in Figure 27 and for sludge liquor in Figure 28, where the trace element content is determined from the average or median value representing a single sample set taken on a given date.

The relationship between the concentration of trace elements for coal (corrected for absorbent) and sludge solids in Figure 27 shows excellent agreement. The band as drawn has a slope of unity of over more than three orders of magnitude, which indicates a directly proportional relationship between the amount of a trace element present in the coal and that found in the sludge.

The comparison for sludge liquors in Figure 28 is supportive of a directly proportional relationship with the process coal, but the confidence of this relationship is far less clear. In this case, the bandwidth is nearly two orders of magnitude, and the point scatter is much greater than for solids. The trace element concentration in the liquor is approximately two orders of magnitude less than that for the solids, and some of the uncertainty associated with precision at lower concentrations may be reflected in this scatter. Nevertheless, allowing for this scatter, it is evident that the slope of the data is identical to that for the solids. In general, the trace element content of the liquor is approximately 0.01 the trace element content of the solids. There is no evidence in these plots for control of trace elements by solubility limitations. If this were so, the datum points in Figure 28 for specific elements would be expected to be along a vertical line representing a saturation concentration independent of coal content greater than that value.

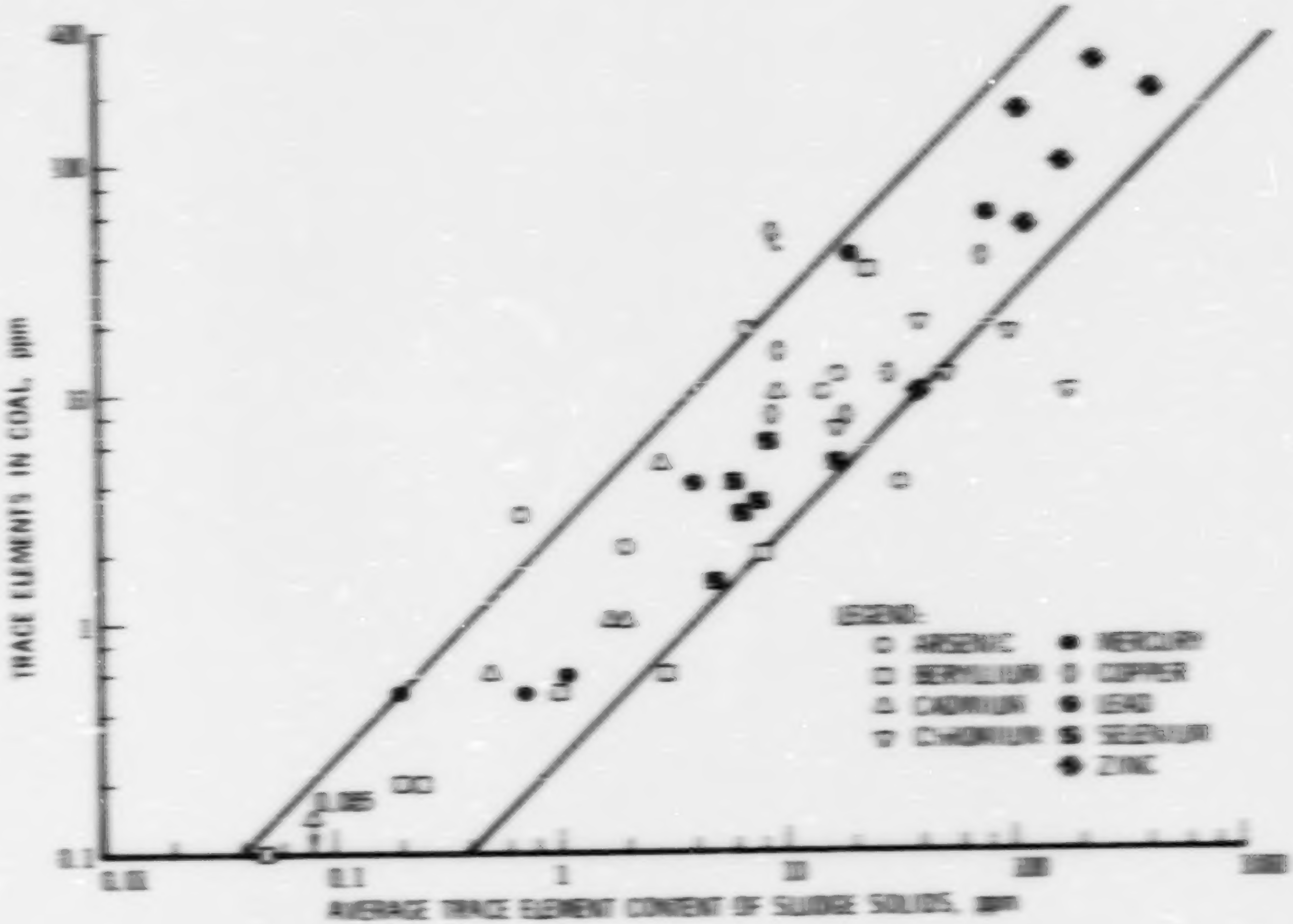

Figure 27. *Average trace element content of sludge solids.*

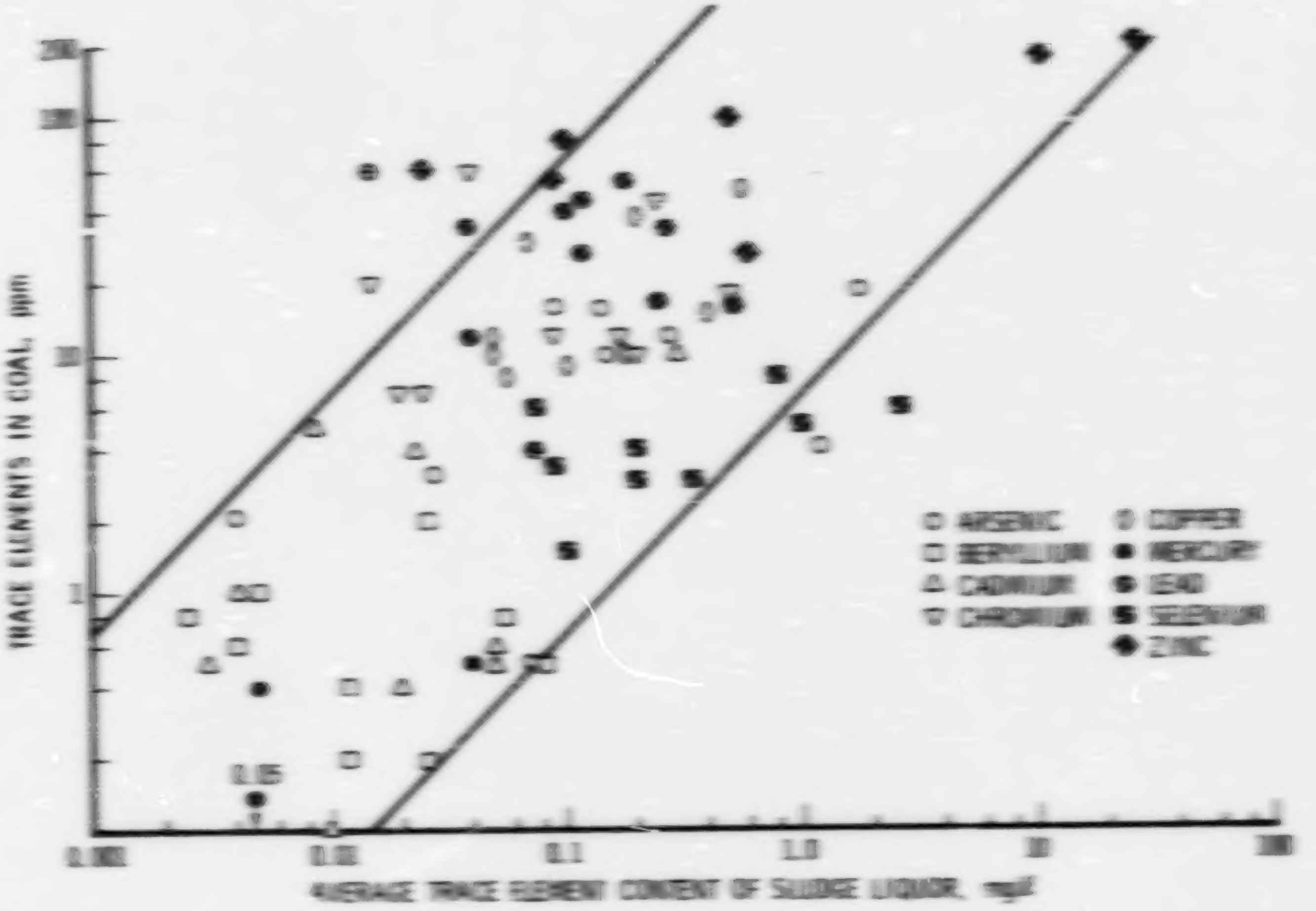

Figure 28. Average trace element content of sludge liquor.

The correlation between coal and sludge is especially significant when evaluated with respect to the range of 3 to 60 percent fly ash in the sludge sampled. Since fly ash is a major constituent in most of the sampled sludges, it would be expected that sludges having higher values of fly ash would have higher values of the trace elements within them. When evaluated point for point, it is revealed, as a general rule, that those sludges with high fly ash content tend to lie on the right side of the band, whereas low fly ash sludges are more generally found on the left side of the band. It is presumed that if the trace element content for each sludge were corrected for relative fly ash content, the data bandwidth would measurably narrow.

In addition to the above considerations, the trace element content in sludge liquors has already been shown to be affected within a system by scrubber pH. If the trace element content for the sludge liquor could be corrected for the differences in pH, a further reduction in data scatter would be evident, and the relationship with coal content would be much more apparent.

In summary, the trace element content of sludge solids and liquors are directly dependent upon the trace element content in the process ingredients, particularly coal; data scatter is explained as a function of the variation in fly ash content in the sludges. In addition, scatter in the liquor data is expected because the scrubber pH has been shown, Section 7.4.4, to influence (but not control) the concentration of trace metals in the system liquors.

7.4.6 Distribution of Trace Elements in Coal Through Combustion

In Section 7.4.5, a correlation was observed between the trace elements concentrated in the FGD sludge and those originating in the coal. The relationship shows that the concentration of trace elements in the sludge had the same relative concentration as that originating in the coal. The bandwidth of the data scatter for solids is about one order of magnitude, and the range of fly ash in the sludges sampled also varied by about one order of magnitude, suggesting that fly ash may be the major source of trace metals in the sludge. Moreover, in evaluating the data bandwidth in Section 7.4.5, it was revealed that sludge with high fly ash content tends to lie on the high side of the band and low fly ash sludge was more prevalently on the low side of the data band.

Chemical analysis of both coal, bottom ash, and fly ash are presented in Appendix D. These data do not provide a sufficiently large data base to perform a materials balance. However, extensive work has recently been reported in the literature (22-25) that can be used for comparison with this study. Since the contribution of trace elements in the sludge are seen to be a consequence of the combustion products of coal, only those elements in fly ash or those existing as vapor in the flue gas can enter the scrubber. No available data even remotely suggest the scrubbing efficacy of the different element vapors from flue gas by a desulfurization scrubber. Thus, only the concentration of trace elements in the fly ash can be used in comparison with trace element concentrations in sludge.

Trace elements are also found in bottom ash and some elements will pass through the system as vapor in the flue gas. Many of the nine trace elements of primary interest in this study (because of limits on them in drinking water criteria) show a disproportionately high contribution to the flue gas stream, either as vapor or ultrafine particulates (typically $<0.1\ \mu m$), based on measured concentrations in the wastes relative to their total concentration in the coal. Of these, mercury in particular is found preferentially in the flue gas (as are sulfur, chlorine, and fluorine). Additionally, arsenic, selenium, cadmium, and chromium appear to be preferentially in the flue gas. Those elements that as oxides are easily and readily found as glass modifiers, such as lead, beryllium, zinc, and copper, are concentrated in the fly ash fraction.

The results of this study are consistent with the trace element distribution studies found in the literature and show that the major source of trace elements found in the sludge originate in the fly ash and possibly, in some cases, from the flue gas. The previous section reveals that a small fraction of the trace element content is in an unsaturated state in the sludge liquor. It is presumed that these metals originate by leaching from the fly ash during the more acid cycle of the scrubbing operation and that the higher concentrations of trace elements in low pH systems reflect this leaching process.

7.4.7 Comparison of Trace Elements in Eastern and Western Coals

The correlation between trace elements in sludge and coal demonstrated in Section 7.4.5 suggests that the trace element content expected in eastern and western scrubbing liquors may differ as a consequence of differences in trace element content of the coals. Figure 29 presents a comparison of the trace element content between the coals analyzed in this study with the analysis of coals by region performed by the U.S. Bureau of Mines (26), U.S. Geological Survey (27), and Illinois State Geological Survey (ISGS)(24). The bar graphs for coal are in the 90+ percent range as presented in a recent EPA report (25); the dots represent the average values from the ISGS study. Individual coal analyses from this study are grouped by region and identified by letter.

The comparison of literature analyses in Figure 29 show that the trace element content from the literature for the Appalachian region coal and interior region coal are nearly identical for most elements in both average value and range, with the exception of cadmium and zinc, which are significantly higher in the interior region coals, and lead where disagreement among investigations is apparent. Comparing the literature values for eastern coal (combined Appalachian and interior regions) with western coal, it is seen that western coals tend to have lower trace element contents in general and significantly lower contents for arsenic, cadmium, mercury, and zinc.

When comparing coal analyses of this study with the literature analysis in Figure 29, it is seen that, with few exceptions, the range of measured values falls within the range for each element as reported in the literature. Moreover, in most cases, the average value from this study lies within

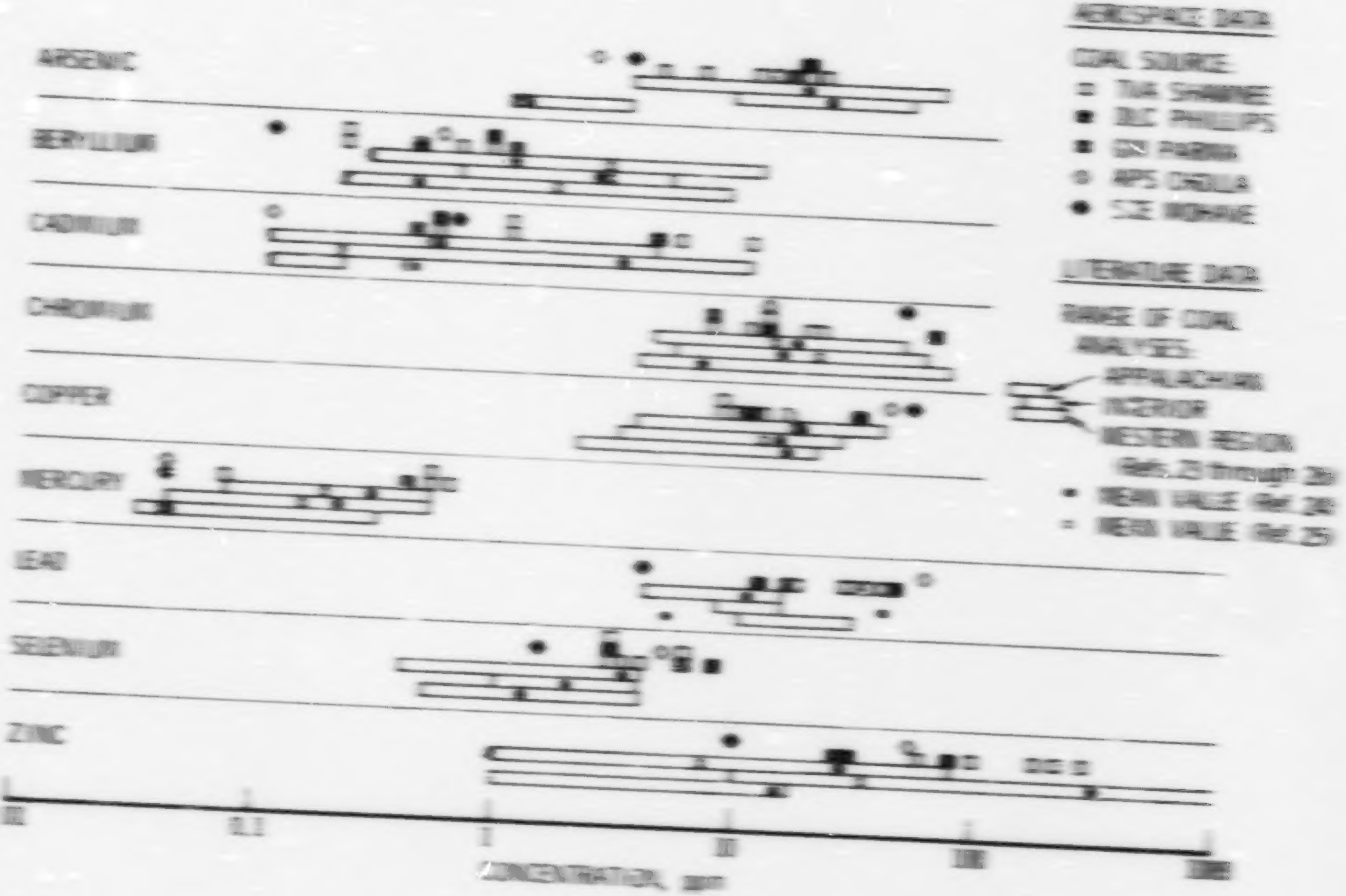

Figure 29. Comparison of coal analyses with literature data.

a factor of two of the average value reported in the ISGS (24) or EPA (25) study. These data show that measured values from western coal for arsenic, cadmium, mercury, and zinc were lower than the measured values from eastern coals. No other element showed a significant difference between regions except for copper, which had high values in the western coal. These high values may be explained by the colocation of the coal fields studied in this report with a major copper-producing region.

Through a comparison of eastern and western coals, one may expect trace element concentrations in the sludge from these coals to differ only in the content of arsenic, cadmium, mercury, and zinc among the elements studied. This study has confirmed this expectation and suggests that the concentration of any element would be found in the sludge at a value relating directly to its concentration in the coal.

SECTION VIII

CHEMICAL SOLUBILITY ANALYSES

The composition of the effluent from the lime and limestone wet scrubbing system is determined by the interactions of species originating in the lime or limestone, flue gas, fly ash, process water, and air.[*] In the liquid phase of the recirculating system, solubility is the primary factor which limits the concentration of each component. From a knowledge of the interaction of the chemical species in each scrubber system and their solubility product constants, it is possible to predict the maximum concentration of each species as determined by its solubility under the specific chemical conditions of the scrubber liquor. A minimum of analytical data is needed, consisting of the pH, the ionic strength, and the concentration of only one principal species with which the liquor is saturated. Although the calculations are not complex, it is advantageous to use the computer to obtain iterative solutions to the equations. The Aerospace Corporation computer program SCRUB was designed to predict maximum concentrations of trace chemical species as a function of the concentrations of major species from solubility data. A program written by the Radian and Bechtel corporations was similar in that it was designed to predict major species concentrations in a scrubber system from thermodynamic data, but the trace chemical species concentrations were not predicted.

8.1 BASIS OF PROGRAM MODEL

Computer program SCRUB was written specifically to calculate the composition of a liquor of known pH and ionic strength and a known concentration of either calcium, or sulfate, or total sulfite, or total carbonate. The liquor was presumed to be saturated with these ions as well as with nine other elements selected because of their potential adverse health effects: beryllium, cadmium, chromium, copper, mercury, lead, zinc, arsenic, and selenium. For sulfite and carbonate, two options were available. Either the liquor was assumed to be saturated with one or both of these ions, or the liquor was in equilibrium with a specified partial pressure of either SO_2 or CO_2 gas, or both. At high pH the saturation assumption is necessary, while at low pH gas phase equilibrium is required to avoid an unrealistically high total CO_2 or total SO_2 content of the liquor. In addition, the liquor may contain magnesium, sodium, or chloride at concentrations which must be specifically measured. Either potassium or nitrate is supplied by the program in an amount necessary for electrical charge neutrality. These latter five species do not enter into the ionic equilibria, except for magnesium at high pH, but contribute to the total ionic strength of the liquor and must be considered for electrical charge balancing.

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[*] Atmospheric O_2 and CO_2 interact with the system liquors where there is prolonged exposure such as in reaction tanks, holding tanks, and clarifiers.

In order to limit the size and complexity of the program, a number of simplifying assumptions have been made in modeling the liquor system. It is known that some of these assumptions will result in systematic inaccuracies, but the intent is to determine the approximate upper limits on the amounts of the trace elements set by their individual solubilities in the liquor. Therefore, it is considered unnecessary to include those factors which would have only minor effects on the solution equilibria but which would add to the complexity of the program. For example, the solubilities of the four calcium compounds of primary interest in the scrubber liquor, namely carbonate, hydroxide, sulfite, and sulfate, have been shown to be only slightly dependent on temperature in the 0 to 100°C temperature region (29). Neither is the water solubility of SO_2 strongly dependent on temperature. Since the scrubber liquor will be within this temperature range and the exact temperature at the time of analysis is usually not recorded, it is unnecessary to include temperature corrections to the solubility product constants. Another assumption is that intermediate ion-product equilibria can be ignored in establishing solubility product constants. This assumption was also made in most of the older measurements found in the literature[*]; therefore, as long as the total amount of each soluble ionic species is being considered, the calculated results will be valid. By using experimentally determined expressions to correct the solubility product constants for the effect of ionic strength of the liquor, it is unnecessary to use activities and activity coefficients in the solubility calculations. The mathematical demonstration of the validity of this simplified treatment of the thermodynamics of these systems is presented in Appendix F.

Program SCRUB contains the additional assumption in that the expected maximum concentration of the cations is the minimum value soluble in the presence of the given concentrations of the anions: hydroxide, carbonate, sulfite and sulfate. Similarly, for the above four anions, as well as the four anions involving the elements arsenic and selenium, concentrations would be calculated using the solubilities of the calcium and magnesium compounds, and the smaller of the two values would be taken as the maximum solubility. This iterative procedure was necessary because the literature does not contain all of the solubility product constants K_{sp} necessary to complete the 10 × 10 matrix of anions and cations. Furthermore, the wide range of K_{sp} values would result in a very "ill-conditioned" matrix which, upon inversion would produce useless solutions to the equations, e.g., negative values of ionic concentrations. In every case, account was taken of the effects of pH on the anion concentration and of ionic strength on the solubility product constant.

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[*] Most ionic interactions are the sources of deviation from ideal behavior of electrolytes, which are accounted for empirically by the mean activity coefficient.

8.3 OPERATIONAL DESCRIPTION

A brief operational description of program SCRUB is given herein starting with a typical case in which the pH, the ionic strength, the partial pressures of CO_2 and SO_2, the calcium concentration, and the concentrations of chloride, magnesium, and sodium are specified input data. All input and output concentrations are in units of milligrams per liter. The partial pressures of the gaseous species are expressed in atmospheres. After checking the selected options, all concentrations are converted to moles per liter; the hydrogen and hydroxide ion concentrations are obtained from the pH; and the calcium and hydroxide concentrations and calcium and chloride concentrations are compared so that the input data will not be in conflict with the respective solubility products. Provisional values of the total sulfite and total carbonate are computed from the partial pressures of CO_2 and SO_2, respectively. Sulfate, total sulfite, total carbonate, total arsenic, and total selenium concentrations are calculated from the calcium and again from the magnesium concentrations using the respective values of K^0_{sp}. The smaller of the two results for each anion is retained in each case. The concentration of each of these anions, including hydroxide, is then used to calculate the solubility of each of the eight cations (excluding calcium and magnesium), and the smallest value for each of the cations is retained. The charge is balanced by the introduction of sufficient nitrate or potassium. If the ionic strength has not been specified, it is computed so that acid dissociation and solubility product constants corrected for the effect of ionic strength can be determined. These values are now used in place of the K^0_{sp} values in a repetition of the calculations beginning with the calculation of H^+ and OH^- concentrations from the pH. If the ionic strength has not been specified, the calculation of each ion concentration (except for the input data for calcium, magnesium, chloride, and sodium) is iterated until the calculated ionic strength is changed by less than 2 percent, whereupon all the ion concentrations are printed.

The operation is quite similar if the concentration of one of the anions, i.e., sulfite, carbonate, or sulfate, is the specified input quantity rather than calcium, except in this case the calcium concentration is calculated from the solubility product constant of the given anion together with its corresponding input concentration. The remaining calculations are the same as for the preceding illustrative case; however, in this case the input anion concentration is the only value that is not altered by the iterative calculations of solubility.

If experimental values of the concentrations of calcium and one or more of the appropriate anions, as well as the pH, are available, each input concentration is treated as a separate case, and the results are averaged to obtain a calculated composition which may be compared with the experimental data.

8.3 TEST OF PROGRAM

A test of the validity of the described program was made by comparing the experimentally determined analytical data for 47 samples of scrubber liquors taken from various locations at 6 power generating stations with the maximum concentrations of major chemical species computed with SCRUB by using experimental values for calcium and for sulfate as input. It was assumed that each liquor was saturated with calcium sulfate (gypsum), although the compositions of the liquors varied considerably. Calcium concentrations ranged from 200 to 3100 mg/ℓ; sulfate concentrations ranged from 700 to 35,000 mg/ℓ; total sulfite concentration ranged from a negligible amount to 3500 mg/ℓ; pH range from 2.7 to 12.8; and ionic strength ranged from 0.06 to 1.6. Agreement between experimental and calculated compositions over these wide ranges of conditions indicates that the program method and thermodynamic constants are valid.

A second test consisted of comparing the calculated concentrations of major species for the same 47 samples with similar calculations of composition resulting from a program originally written by The Radian Corporation (29) and later modified by the Bechtel Corporation. This program only calculates the concentrations of the major species, and the methods used differ markedly from those of the Aerospace program SCRUB. However, by comparing the experimental values for calcium and sulfate with the results calculated with the two independent programs, it is possible to corroborate the assumption of saturation and to check the validity of the approximations made in SCRUB. The Radian-Bechtel (R-B) program makes few approximations and solves a system of nonlinear simultaneous equations to obtain the best-fit composition of the sample. For this reason, more input data are required. Corrections are made for temperature, pH, ionic strength, activity coefficients, and water of hydration. As a result, the program requires considerably more internal theoretical information.

8.3.1 Comparison of Experimental and Calculated Major Species

Calculated calcium and sulfate concentrations were compared with measured values for each of the 47 liquor samples. For the 47 samples, the mean ratio of the experimental calcium ion concentration to the calcium ion concentration calculated with the R-B program was 1.01. This ratio ranged from a high value of 2.19 to a low of 0.30, and the standard deviation was 0.33. The mean ratio of the experimental sulfate ion concentration to the sulfate ion concentration calculated with the R-B program was 1.02. The high value of this ratio was 2.00; the low value was 0.44; and the standard deviation was 0.28.

With the Aerospace program SCRUB using the data from the same 47 samples, the mean experimental-calculated concentration ratio was 1.11. The high and low values of this ratio were 2.17 and 0.39, respectively, and the standard deviation was 0.43. With the Aerospace program, the experimental calculated concentration ratios were equal for both calcium and sulfate ions since both ratios are identical to the product of the experimental calcium ion concentration and the experimental sulfate ion concentration divided by the corrected solubility product constant.

The measured concentration of either calcium or sulfate has a direct influence on the calculated concentration of the other. If the measured concentration of either calcium or sulfate is seriously in error, then the calculated concentrations of both ions will not agree with their experimental counterparts. Therefore, it is possible to identify analytical data that are likely to be in error. For six samples, results of calculations with both computer programs showed that the analyses of six species were probably in error. When the values of these six concentrations were arbitrarily altered to be consistent with the data base, the mean concentration ratios were decreased to 1.04 (±0.29) with the Aerospace program and to 1.01 (±0.26) with the R-B program.

The constancy of these ratios and their close approximation to unity furnish good evidence that the liquors were saturated with calcium sulfate. In only a few samples was there similar evidence of saturation with calcium sulfite. No comparable analytical data were available to ascertain whether the liquors were saturated with calcium carbonate. For liquors with low pH values, saturation with either calcium sulfite or calcium carbonate is improbable.

Figures 30 and 31 are pH plots* of the experimental concentrations of calcium and sulfate and the values calculated with the two programs for direct comparison of the data for each of the 47 samples. The concentration ratios were plotted against pH, ionic strength, calcium concentration, and sulfate concentration in a search for correlations. These ratios did not appear to depend on any of these parameters within the ranges tested, as shown by the data in Appendix F (Figures F-1 through F-3).

8.3.2 Comparison of Experimental and Calculated Trace Species

A comparison of experimental and calculated concentrations of minor species may not constitute a suitable test of the validity of the Aerospace calculations because there is no assurance that the liquors were saturated with all, or any, of the nine trace elements. Nevertheless, these comparisons have been made using the experimentally determined major species concentrations as input data. In Appendix F (Figures F-1 through F-12), the logarithms of the concentrations of the nine elements (in units of milligrams per liter) are plotted against pH for both experimentally determined concentrations of trace elements and for concentrations calculated with the Aerospace program. It is evident that for all nine elements the pH of the liquor was the factor that determined the calculated solubility, at least over a portion of the pH range. For arsenic (Figure F-4 in Appendix F),

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*It is not intended to demonstrate a correlation of the data with pH. The solution pH is used as a more informative identifier than a sequential sample number.

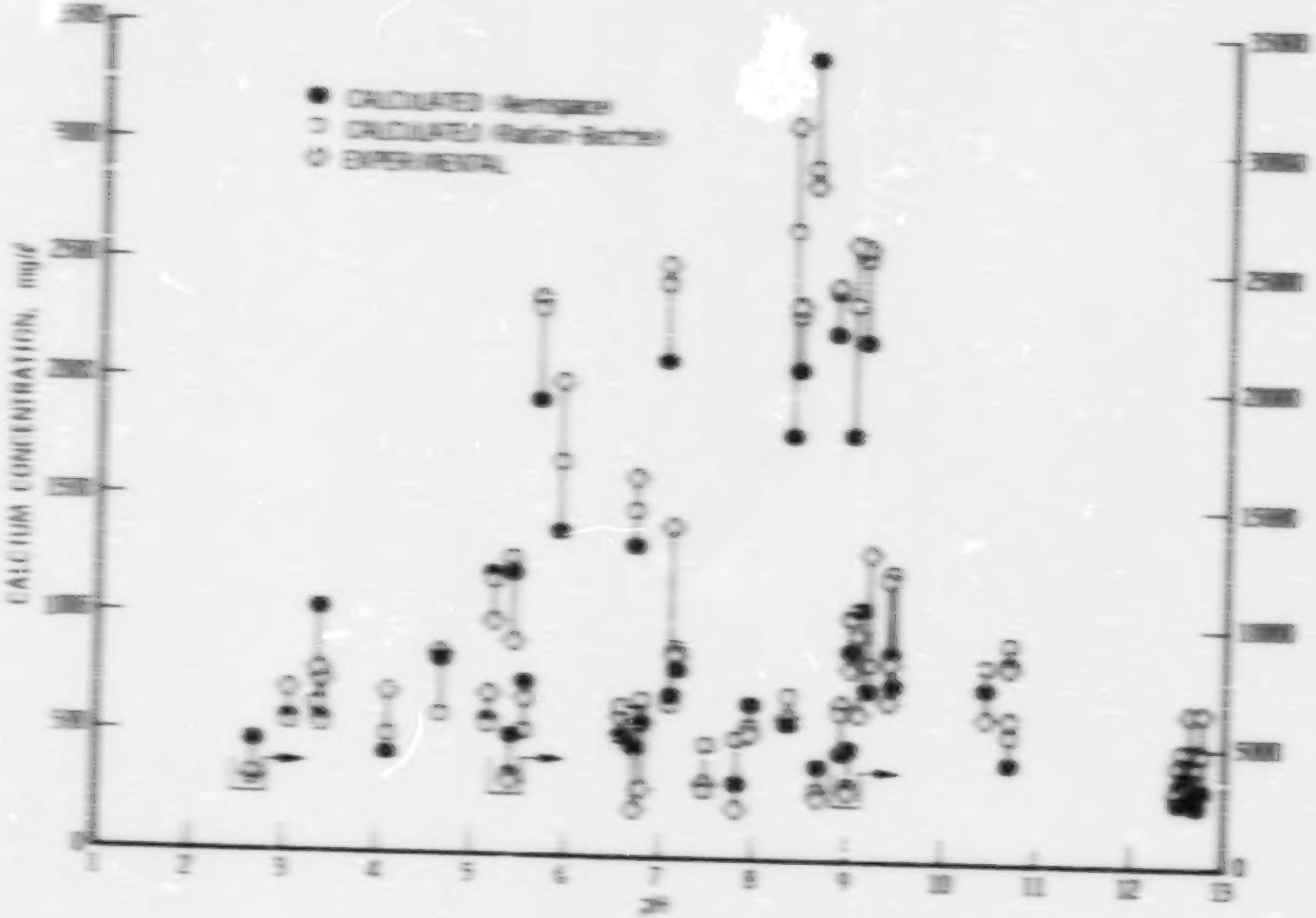

Figure 38. Comparison of experimental calcium concentration and concentrations calculated with two computer programs.

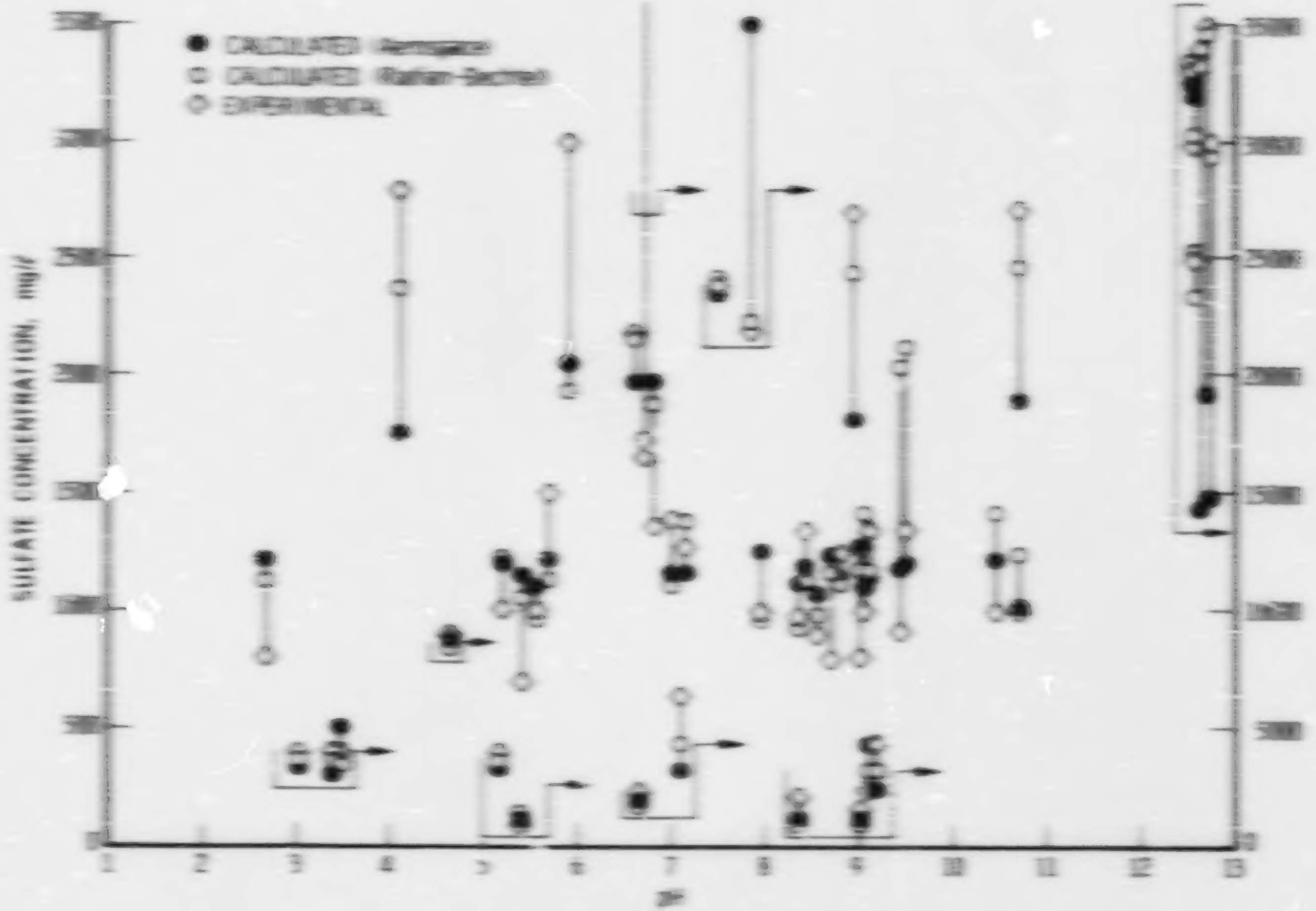

Figure 31. Comparison of experimental sulfate concentration and concentrations calculated with two computer programs.

this pH range was below 9.5. Above 9.5, all of the arsenic was available for precipitation as the arsenate (or arsenite) of calcium. A similar explanation exists for the form of the calculated curve for selenium (Figure F-11 in Appendix F). Above pH 6, the selenite concentration was not reduced by the formation of biselenite ions. For beryllium, chromium, copper, mercury, and zinc (Figures F-5, F-7 through F-9, and F-12 in Appendix F), the applicable pH range extended over the entire range of experimental measurements from pH 2.7 to 12.8. Cadmium (Figure F-6 in Appendix F) was precipitated by hydroxide ions above pH 10 and at a lower pH by carbonate ions originating from the atmospheric CO_2 or limestone. Below pH 7.5, the concentration of carbonate was reduced by the formation of bicarbonate. The calculated curve for the solubility of lead (Figure F-10 in Appendix F) was complicated by its precipitation by three agents. Above pH 9, hydroxide ions controlled the lead concentration; between pH 9 and pH 7, carbonate ions originating from atmospheric CO_2 or limestone were controlling. Similar to cadmium, below pH 7.5, the formation of bicarbonate decreased the available carbonate. Below pH 7, lead was precipitated by sulfate ions, the concentration of which was reduced by the formation of bisulfate below pH 3.

The experimental concentrations of the nine elements indicate no apparent dependence on pH. With several exceptions which will be cited, the experimental data for all nine elements scattered within a band which spanned approximately two orders of magnitude from 0.4 to 2×10^{-3} mg/ℓ, except for selenium (2 to 2×10^{-2} mg/ℓ) and zinc (1 to 1×10^{-2} mg/ℓ). For lead and mercury, the bandwidth was approximately three orders of magnitude, from 2 to 4×10^{-3} mg/ℓ for lead and from 0.2 to 2×10^{-4} mg/ℓ for mercury. One sample (pH 7.15) was disregarded since the analyses for 3 of the 9 elements were higher, by a factor of 10, than any of the remaining values for those elements. This sample was the first (chronologically) to be analyzed, so the results may have been in error because of uncertainties in experimental procedures.

For arsenic and selenium, the experimental data are all lower than the calculated solubility by at least three orders of magnitude. This most probably was the result of insufficient material to exceed the solubility product constant so that no precipitation occurred. For the other seven elements, the experimental data are lower than the calculated curves below a characteristic pH but are above the calculated curves at a higher pHs. This characteristic pH varies from a low value (for mercury) of 4.5 to a high value (for cadmium) of 10.5.

Since solubilities greater than the theoretical values do not correspond to a condition of thermodynamic equilibrium, it is well to consider alternative explanations of the data. The observed invariance of the experimental data over this broad pH range may cause one to suspect that the elements were not in solution. Instead, the ions of these elements may have been adsorbed on the surfaces of dispersed colloidal particles and were analyzed as though they were in solution. The invariance of the data with pH would then be the result of approximately constant colloidal particle densities for all the samples. Additional experiments are necessary to test this hypothesis.

Other explanations such as systematic errors in analysis, due to instrument bias or due to contamination seem unlikely since these results are a correlation of analyses from four independent laboratories (Appendix C).

8.4 SUMMARY AND CONCLUSIONS

Data from 47 samples of effluent from lime and limestone scrubbers at 6 power generating stations have been analyzed and compared with calculations based on solubility equilibria. In every case, there is evidence that the liquor was saturated with calcium sulfate. In only a few samples, is there evidence of saturation with calcium sulfite, presumably because in the other samples the sulfite had ample time to be oxidized by atmospheric oxygen. No analytical data were available to resolve the question of calcium carbonate saturation because saturation levels were typically lower than detection levels of carbonate.

Furthermore, for both calcium sulfite and calcium carbonate, the question of saturation of the scrubber liquors cannot be completely resolved by analytical data unless the initial composition of the gaseous phase in contact with the liquor is maintained. Both sulfur dioxide and oxygen partial pressures, along with pH and ionic strength, determine the equilibrium concentration of total sulfite in a saturated liquor, and carbon dioxide has a similar role in determining the equilibrium concentration of total carbonate.

For the nine trace elements evaluated, the experimental data give inconclusive evidence on the question of saturation. Specifically, trace element concentrations in liquors were invariant with changes in pH and major anion species. Further experiments are needed to reconcile apparent discrepancies between experimental and calculated results.

With computer program SCRUB, one can calculate the composition of scrubber liquor from the pH, the ionic strength, and the concentration of one ion involved in saturation equilibrium. An operational description of this program has been given. The results of its application to the 47 liquor samples demonstrate its usefulness for predicting maximum concentrations of components of scrubber liquors based on solubility considerations.

SECTION IX

EVALUATION OF THE ENVIRONMENTAL ACCEPTABILITY OF FGD SLUDGE

The laboratory data presented in this report reveal the phenomenological behavior of flue gas desulfurization (FGD) sludges to be expected in field disposal. The behavior characteristics have been separated into chemical and physical properties, and experiments have been conducted in a manner so as to simulate closely the environmental conditions expected in actual field disposal. Thus, the range of experiments have included every type of disposal considered likely from an economic point of view, and most properties have been determined on the basis of environmental acceptance.

9.1 OVERVIEW

It would be desirable to evaluate all disposal conditions on an absolute basis. However, the current lack of appropriate criteria regulating FGD sludge disposal does not allow an absolute definition of "environmental acceptability." Moreover, the environmental impact of FGD sludge disposal will be dependent not only on the properties of the sludge, but also on the geological and hydrological conditions of the disposal sites. Thus, an evaluation of the environmental impact of FGD sludge must be made solely on the anticipated behavior of the sludge under the various alternative methods of disposal, without specifically defining the environmental acceptability of the sludge. The following sections discuss the expected impact of FGD sludges on the environment with respect to the range of properties observed in this study. It is presumed that the range of properties observed in the sludges sampled are representative of the sludges that are being and will be produced. In the small sampling of this study, an attempt was made to provide representation for eastern and western coals; lime, limestone, and double-alkali systems; sludges with and without fly ash; and systems operating at both high and low pH. Although not every combination of variables could be included, it is believed that the following discussions will be valid for a majority of the sludges that will require disposal.

In order to evaluate the environmental impact of alternative disposal techniques for FGD wastes, it is necessary to assess the various routes by which chemical pollutants may enter the environment from a disposal site and to determine the relative mobility of the various chemical species with respect to their environmental accessibility. Thus, in addition to chemically characterizing FGD sludges, this task effort includes experimental determination of the potential pollution hazard that is inherent in each

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of the various disposal techniques. The assessment of the potential pollutant hazard includes considerations of the chemical state of the pollutant and the route by which it may enter the environment.

9.2 ROUTES OF ACCESSIBILITY OF POTENTIAL CHEMICAL POLLUTANTS TO THE ENVIRONMENT

The disposal of FGD wastes makes possible several alternative routes by which chemical constituents in the desulfurization wastes may enter the environment. The facilities generating these wastes are described in Appendix B. As previously discussed, the quantitative identification of chemical constituents in the wastes has been determined (Section VII), and correlations between the chemical constituents and the variables of each system have been made such that the pollutant potential of each waste can, for the most part, be anticipated (Section 7.4). In this section, the various routes by which these pollutants can enter the environment are explored so that the actual pollutant potential can be assessed relative to the techniques by which the waste is disposed. Additionally, through experimentation, the capability of a waste for creating a pollution problem is determined. The environmental conditions simulated by each experiment are presented, as well as the environmental consequences of each simulated method of disposal.

The route of access of chemical pollutants to the environment from FGD waste can be through either air or water. The untreated waste is disposed of as sludge a mixture of solids and occluded liquor. The introduction of potential pollutants into the environment through air may occur either by vaporization of the pollutant from the solid or liquor phase by mass transfer of spray from the surface of a wind-whipped disposal pond or by blowing dust from an air-dried site. Pollutant introduction (through water) into the environment from managed disposal sites can occur by leaching the sludge with rainwater, by both displacement of the occluded liquor and dissolution of the solid phase.

In the case where the sludge is treated by one of several techniques to convert it into a solid material, the opportunities for a chemical pollutant to enter the environment is more limited. Pollutant introduction into the air by vaporization is minimized, and by spray transfer it is avoided except where water is allowed to collect on the surface of a solid mass. If weathering has produced a powdery surface which is left exposed, blowing dust could be a problem. Pollutant introduction through water by leaching is minimized if the solidified sludge offers greater resistance to water passage. Pollutant introduction by runoff water can also be reduced if the solidified waste does not release chemical constituents as readily as untreated waste. In every potential route for environmental pollution by the chemical constituents of FGD wastes, the disposal of solidified waste offers the opportunity to minimize the pollution potential relative to disposal of untreated waste. The cost effectiveness of solidification relative to untreated waste disposal by alternative methods will be dependent upon site-specific conditions.

The following sections describe the experiments and results conducted to evaluate the pollution potential of various methods of disposal.

9.2.1 Pollution by Vaporization

The potential for vapor loss of a particular chemical species is dependent upon a number of factors, but primarily the vapor pressure of the species and the effect of temperature on vapor pressure. The most severe condition that could exist under normally occurring environmental circumstances is that in which a sludge dries and increases in temperature under direct solar heating. Under extreme conditions, the surface of the sludge may reach temperatures as high as 150°F (66°C), and these temperatures may be adequate to vaporize certain chemical species.

For determination of whether volatile chemical species may sublime from the surface of a disposal basin while being heated by solar energy, the clarifier underflow from the TVA Shawnee limestone system (sampled on 1 February 1973) was dried thermally in such a way that the volatiles were analyzed with a quadrupole mass spectrometer. At temperatures to 180°F (82°C), only water was observed; at increasing temperatures, the water signal dropped off; at 650°F (334°C) strong signals from SO_2 and CO_2 were present from dissociation of the sulfate and carbonate phases. No other volatile species was observed.

The sensitivity of the quadrupole mass spectrometer was determined from the measurement of free vaporization of elemental mercury. It was found that a partial pressure of 2×10^{-7} atm of mercury could be detected. Thus, vaporization of mercury (bp 357°C) or mercuric chloride (bp 302°C), if it had occurred, was below this level of detection. The sensitivity for other chemical species present in the sludge by mass spectrometry was comparable or even higher. Thus, the lack of signal from any chemical species indicated that its presence in the vapor phase over the sludge was at a value of less than 10^{-7} atm. This value is many orders of magnitude lower than that required to create an environmental hazard. It was concluded, therefore, that environmental pollution by vapor phase loss to the atmosphere does not occur even under extreme climatic conditions.

9.2.2 Pollution by Wind-Whipped Spray

An alternative method of disposal of untreated sludge may be one in which the sludge is ponded such that water collects on the sludge surface; another method of disposal is that in which the sludge is chemically treated, disposed of in a basin, with rainwater allowed to collect on its surface. In either case, strong winds blowing across the surface of the pond or basin may produce a spray containing the chemical constituents of the surface water. Under most conditions, the fine spray particles fall to the earth within a mile of the basin. Environmental pollution in this case, then, may be restricted to contiguous agricultural areas, with the extent of pollution particles dependent upon the concentration of chemical species in the pond surface water. Values for pond supernate quality can be obtained from the

TVA Shawnee Field Disposal Evaluation Project (2). Wind-spray or wind-blown dust (at sites where supernate has evaporated or where fixed sludge landfills are exposed to the air) will be a problem only in certain specific areas. In these areas, proper site management should be maintained to prevent environmental pollution.

9.2.3 Pollution by Runoff

The potential environmental pollution by rainwater runoff from the surface of FGD sludges exists through the action of surface leaching of chemical constituents and from erosion of particulates from the surface. Subsequently, it can affect either surface waters if the runoff flows directly into streams, or groundwater if the runoff is allowed to percolate through adjacent land. This applies to sludges that are disposed of as a landfill, either above or below grade. At this time, only chemically treated sludges are being disposed of operationally as described above. When treated sludge is disposed of by this method and the site is managed to facilitate landfill operations, such as placement and compaction, rainwater is not allowed to stand on the surface and, therefore, runs off. The potential environmental effects of this runoff would be of concern.

The environmental concern for these sites results from the fact that freshly treated sludges could produce relatively high concentrations of suspended and dissolved solids in the runoff compared with those from a cured material. Since freshly treated material is added to the site continuously, the concern for the quality of the runoff would exist throughout the development period of the landfill. Currently, a runoff collection ditch leading to a siltation pond is used to prevent pollution from suspended solids; the collection of water from a major portion of the landfill area allows for dilution of excessive dissolved solids from local areas of the site containing freshly treated sludge. Freeze-thaw cycling may periodically create runoff problems by exposing new surface areas to rainwater; therefore, a compacted overburden of soil is desirable for completed portions of the landfill.

These observations represent only a limited examination of runoff conditions. Current programs by private firms and the EPA are expected to produce a better understanding of these potential problems.

9.2.4 Pollution by Rainwater Leaching of Untreated Wastes

The most serious form of pollution potential exists as a consequence of the action of rainwater leaching through a disposal basin. In the case of untreated sludge, this pollution potential can exist as a consequence of most disposal techniques because the disposal basin is designed to impound rainwater whether or not the disposal technique is by ponding. Water percolates through sludge whenever freestanding water collects on its surface. The amount of leachate that percolates through the sludge depends upon the permeability of the sludge, the permeability of the basin subsoil, and the amount of water made available to the basin either by rainfall or through ponding. The quality of the leachate depends on the availability of chemical species to the percolating waters.

Sludge normally contains occluded liquor from the scrubbing process in an amount representing 35 to 80 percent by weight of the total sludge, depending upon the extent of dewatering. Most of this occluded liquor is flushed from the sludge by the first three pore volume displacements (PVD) of percolating water; thereafter, the quality of leachate is dependent upon the solubility of the solid phase of the sludge. The determination of the quality of leachate from untreated sludge as a function of the amount of water passing through it is described in the following experiments.

Experimental Procedure

Two sets of experiments were conducted. The first set used 100 grams of dried sludge packed into 4-cm glass columns through which 3.6 liters of water were allowed to pass. A set of three columns was packed for each sludge tested, representing the TVA Shawnee limestone sludge, the Arizona Public Service (APS) Cholla limestone sludge, the Duquesne Light Company (DLC) Phillips lime sludge, the General Motors (GM) Parma double-alkali sludge, and the Southern California Edison (SCE) Mohave limestone sludge. Leaching water (unbuffered) adjusted to pH 4, 7, and 9, with either HCl or NaOH, was used on each set of columns. The leaching water and the leachate were allowed to react with air so as to simulate aerobic conditions.*

On the basis of the results of the first experimental set, the second set of leaching experiments were conducted, simulating anaerobic conditions.* These experiments duplicated the first except that the leaching water and leachate were protected from interaction with the atmosphere; 200 grams of dried sludge was used in 6-cm columns, and the leaching water of pH 7 only was used.

In the first experimental set, leachate analysis was performed on the first 600 mℓ of leachate collected and at increments of 750 mℓ thereafter. In the second set of experiments, analysis was performed on the 1st,

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*Whether leaching water or leachate will be aerobic or anaerobic is dependent upon the sludge and site conditions. Aerobic leaching water can result from supernate equilibrium with the atmosphere; however, subsequent percolation through a sulfite sludge can create an anaerobic condition in the leaching water. The resultant leachate can remain anaerobic in the subsoil; however, if the soil is plugged by filtering of fine and colloidal particles from the sludge and penetration through this filter zone is slower than permeation through the soil, the opportunity exists for the creation of air voids in the soil. In this case, the leachate may become aerobic. In field conditions, all four combinations of aerobic and anaerobic leaching water and leachate are possible.

2nd, and 3rd PVD, and then on the 15th, 30th, and 60th PVD. Pore volume was calculated from the mass and volumes of each packed column. In both experimental sets, analyses were performed for arsenic, beryllium, cadmium, chromium, copper, lead, mercury, selenium, zinc, chloride, fluoride, sulfate, pH, and TDS.

Results of Experiments

The results of the aerobic experiments are presented in Figures 32 through 36. A single curve is presented for each species, representing the median value of concentration from the three values of pH for leaching water used on each sludge type. The analytical results indicate no discernible difference between the columns as a result of differences in the starting pH of the leaching waters, except for certain trace elements as shown in the curves. Moreover, the median value from the three columns used as replicates provide a high level of confidence to the accuracy of the data. The curves are normalized to the concentration of the first pore volume which essentially reflects the concentration of occluded mother liquor. Major species and trace metals existing at high concentration (≥0.1 mg/ℓ) are presented from which typical behavior can be observed. For most trace elements existing in low concentrations in the liquor, the concentration in the leachate dropped below the detection limit of the test method after only a few PVD.

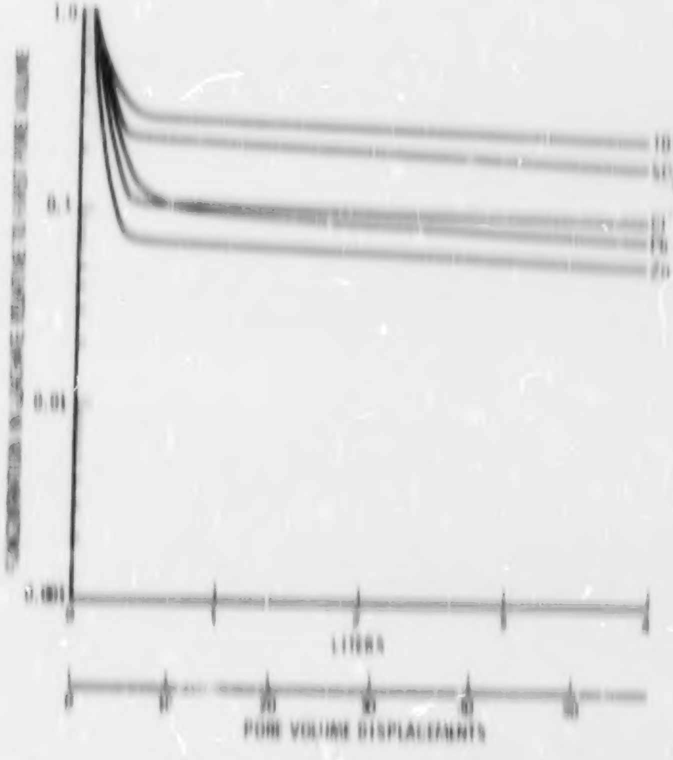

Figure 32. Analysis of leachate from TVA Shawnee limestone sludge: aerobic conditions.

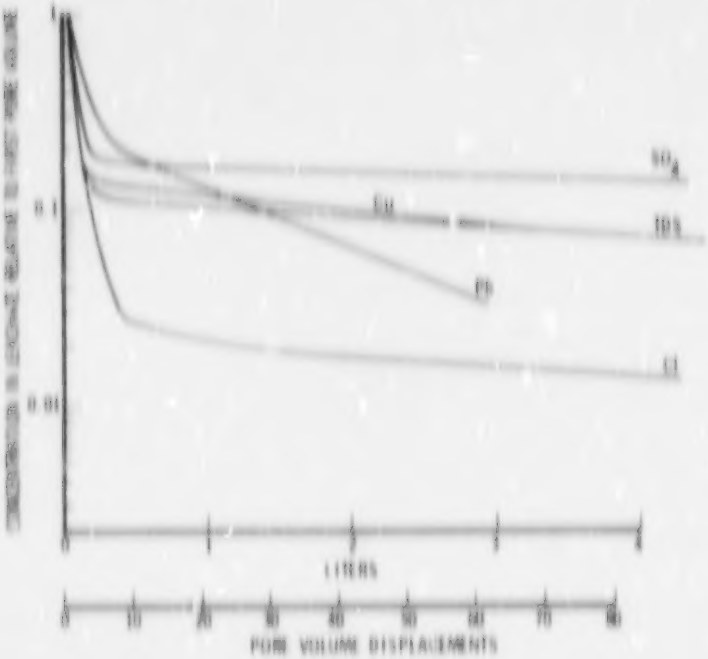

Figure 33. Analysis of leachate from SCE Mohave limestone sludge: aerobic conditions.

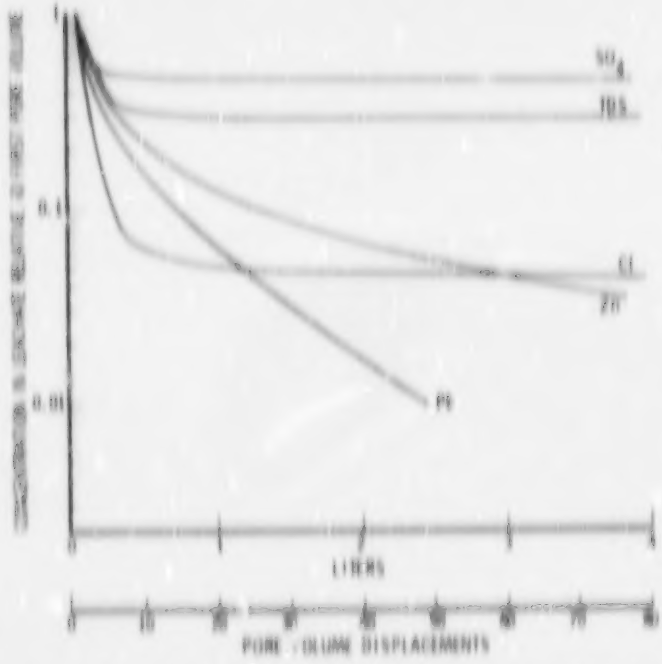

Figure 34. Analysis of leachate from DLC Phillips sludge: aerobic conditions.

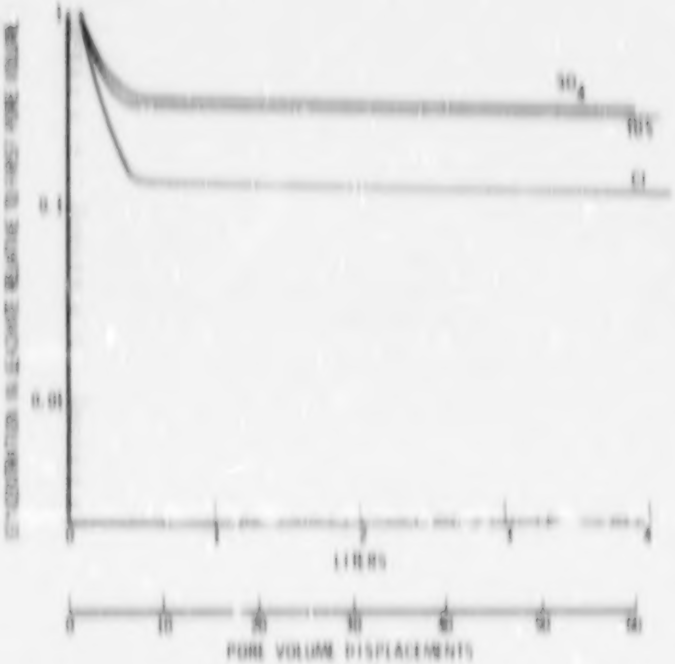

Figure 35. Analysis of leachate from APS Cholla sludge: aerobic conditions.

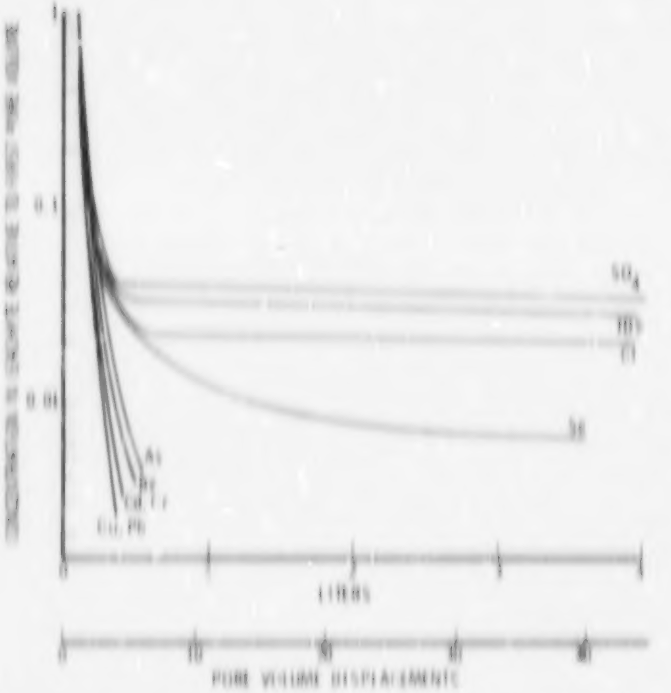

Figure 36. Analysis of leachate from GM Parma sludge: aerobic conditions.

The results of the anaerobic leaching experiments are presented in Figures 37 through 39. These curves are from single columns and obtain their reliability from sequential pore volume analyses. A comparison of results from both the aerobic and anaerobic leaching columns is given in Tables 19 through 23. The concentration of major and trace species is given after the 1st and 50th PVD and is compared with the concentration of the mother liquor of each scrubbing system.

From an overall assessment of the leaching data, it was determined that for each of the major species, represented by sulfate, chloride, and TDS analysis, the concentration decreased rapidly during the first few pore volumes, and in most cases 90 percent of the decrease in concentration of the leachate between the 1st and 50th PVD had taken place at the completion of the 3rd PVD. A similar observation can be made for trace elements with the exception that some elements did not show the sustaining concentration level after the initial pore flushing, as was seen for major species. This behavior may be due to the fact that trace amounts are more difficult to flush from the system, or the observed behavior may be only the result of greater uncertainty in the analytical data because of their low concentration, or perhaps some trace elements are present as fine particulate matter which continues to be flushed.

When comparing aerobic and anaerobic leaching, it would appear from the figures that a greater drop in concentration occurs in the anaerobic

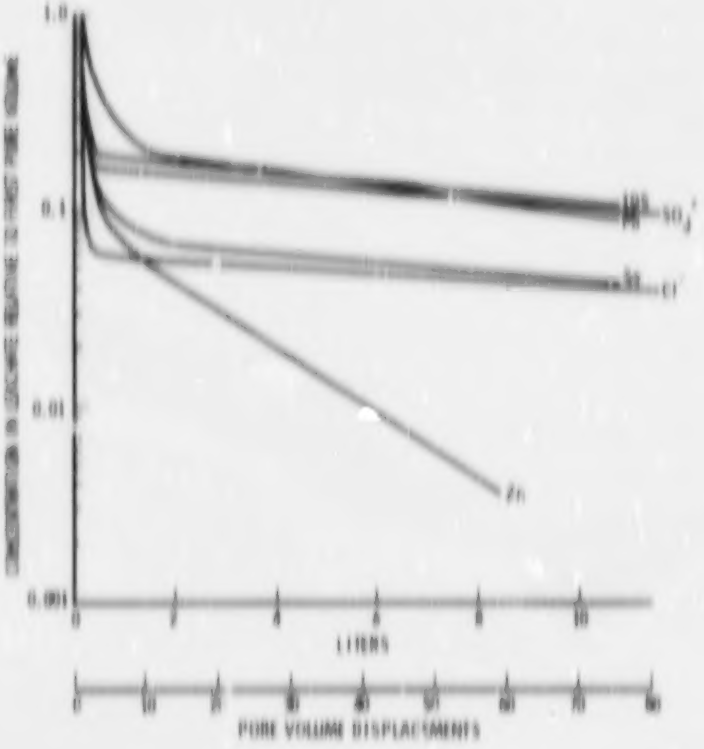

Figure 37. Analysis of leachate from TVA Shawnee limestone sludge: anaerobic conditions.

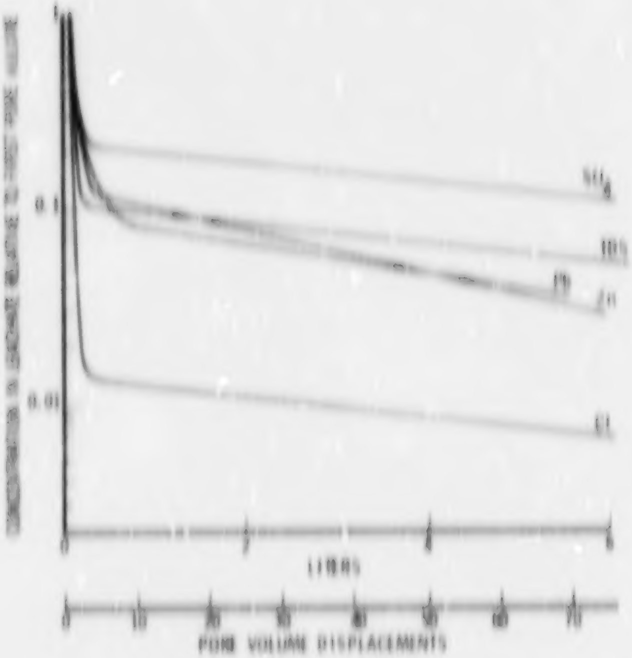

Figure 18. Analysis of leachate from SCE Mohave limestone sludge: anaerobic conditions.

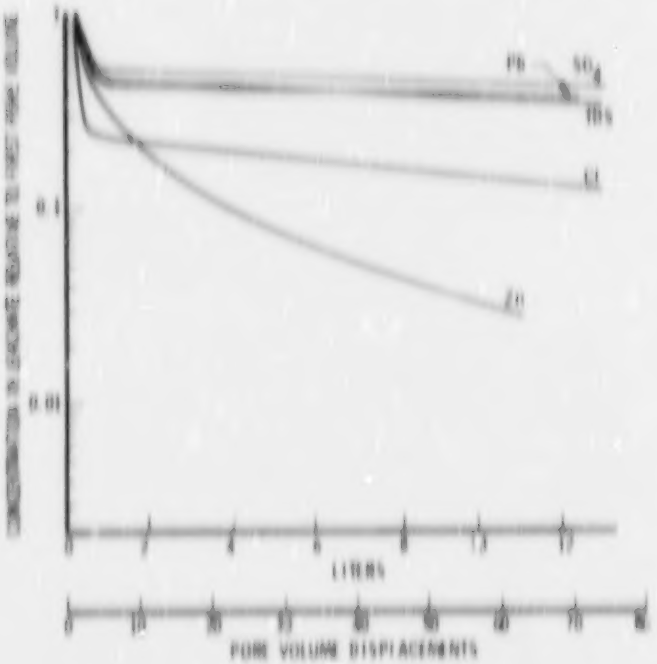

Figure 19. Analysis of leachate from DLC Phillips sludge: anaerobic conditions.

TABLE 19. COMPARISON OF CHEMICAL CONSTITUENTS IN SLUDGE LIQUORS WITH LEACHATE AFTER 1 AND 50 PVD: TVA SHAWNEE LIMESTONE SLUDGE

Constituent	Sludge Liquor, mg/ℓ[a]	Aerobic Conditions, mg/ℓ		Anaerobic Conditions, mg/ℓ	
		1st PVD[b]	50th PVD[b]	1st PVD	50th PVD[b]
As	0.14	0.06	0.01	0.06	<0.004
Ba	0.054	0.008	0.004	--	--
Cd	0.003	0.007	<0.001	0.035	0.003
Cr	0.09	0.025	0.003	0.07	0.015
Cu	0.01	0.007	0.010	0.05	<0.02
Pb	0.25	0.12	0.01	0.47	0.055
Hg	<0.05	0.05	<0.00005	0.005	0.0004
Se	--	0.03	0.006	0.20	0.01
Zn	--	0.85	0.045	0.60	0.01
Cl	2250	1350	120	1700	70
F	6.2	2.7	<0.2	10.8	1.1
SO_3	80	18	25	--	--
SO_4	10,000	6500	1200	9000	1000
pH	8.3	4.7	5.0	8.5	7.4
TDS	15,000	10,500	2400	12,800	1600

[a] Liquor analysis on clarifier underflow.

[b] Values taken from curve.

TABLE 26. COMPARISON OF CHEMICAL CONSTITUENTS IN SLUDGE LIQUORS WITH LEACHATE AFTER 1 AND 50 PVD: SCE MOHAVE LIMESTONE SLUDGE

Constituent	Sludge Liquor, mg/ℓ	Aerobic Conditions, mg/ℓ		Anaerobic Conditions, mg/ℓ	
		1st PVD	50th PVD	1st PVD	50th PVD
As	0.03	0.012	<0.004	<0.004	<0.004
Ca	26,500				
Ba	0.02	0.013	0.004	--	--
Cd	0.05	0.011	0.001	0.05	<0.004
Cr	0.25	0.05	0.003	0.05	<0.015
Cu	0.56	0.11	0.010	0.07	<0.03
Pb	0.04	0.15	<0.001	1.7	0.08
Hg	<0.005	0.001	<0.00005	<0.0005	<0.00005
Se	0.12	0.07	0.004	0.034	0.004
Zn	0.18	0.060	0.045	2.7	0.13
Cl	28,000	7700	130	7500	65
F	30	7.1	<0.2	1.6	1.4
SO_3	1.5	0.6	0.3	0.	0.2
SO_4	25,000	8000	1300	8000	1100
pH	6.7	6.0	4.5	7.38	7.45
TDS	92,500	24,300	2100	23,000	1700

TABLE 21. COMPARISON OF CHEMICAL CONSTITUENTS IN SLUDGE LIQUORS WITH LEACHATE AFTER 1 AND 50 PVD: DLC PHILLIPS LIME SLUDGE

Constituent	Sludge Liquor, mg/ℓ	Aerobic Conditions, mg/ℓ		Anaerobic Conditions, mg/ℓ	
		1st PVD	50th PVD	1st PVD	50th PVD
As	0.09	0.03	0.004	0.01	0.003
Ba	0.012	0.004	<0.003	--	--
Ca	2855	--	--	--	--
Cd	0.023	0.003	<0.001	0.004	0.001
Cr	0.040	0.005	<0.001	0.04	<0.015
Cu	0.07	0.035	0.008	0.04	<0.01
Pb	0.18	0.12	<0.001	0.10	0.04
Hg	0.05	0.0006	<0.00005	0.0004	<0.00005
Se	0.08	0.07	0.007	0.02	0.001
Zn	0.09	0.51	0.03	0.50	0.02
Cl	2700	2400	110	415	65
F	2.6	1.7	0.8	2.4	1.0
SO_3	27	--	--	--	0.2
SO_4	3150	2700	1250	2003	900
pH	7.11	4.98	4.90	7.80	9.65
TDS	9400	7800	2200	3500	1350

TABLE 22. COMPARISON OF CHEMICAL CONSTITUENTS IN SLUDGE LIQUORS WITH LEACHATE AFTER 1 AND 50 PVD: APS CHOLLA LIMESTONE SLUDGE

Constituent	Sludge Liquor, mg/ℓ	Aerobic Conditions, mg/ℓ	
		1st PVD	50th PVD
As	<0.004	<0.004	<0.004
Ca	2670	--	--
Be	0.18	0.007	0.004
Cd	0.009	0.001	<0.001
Cr	0.21	0.019	0.002
Cu	0.19	--	0.01
Pb	0.01	0.016	<0.001
Hg	0.13	0.00008	<0.00005
Se	2.5	0.05	0.05
Zn	0.07	--	0.04
Cl	1430	900	110
F	0.7	2.4	6.1
SO_3	0.9	22	9.0
SO_4	4400	3500	1150
pH	4.3	4.6	5.9
TDS	9100	6500	1900

TABLE 23. COMPARISON OF CHEMICAL CONSTITUENTS IN SLUDGE LIQUORS WITH LEACHATE AFTER 1 AND 40 PVD: GM PARMA DOUBLE-ALKALI SLUDGE

Constituent	Sludge Liquor, mg/ℓ	Aerobic Conditions, mg/ℓ	
		1st PVD	40th PVD
As	<0.004	0.20	<0.002
Be	<0.005	0.32	<0.004
Ca	640	- -	- -
Cd	<0.02	0.87	<0.001
Cr	<0.02	0.95	<0.001
Cu	0.06	1.8	<0.01
Pb	0.52	1.76	<0.01
Hg	0.0005	<0.0005	<0.00005
Na	20,000	- -	- -
Se	0.075	0.29	0.010
Zn	0.59	- -	0.04
Cl	5200	4750	95
F	58	22	0.2
SO_3	140	48	30
SO_4	35,000	31,000	1100
pH	12.7	8.1	6.1
TDS	65,000	58,000	1650

leaching condition than in the aerobic condition, although for the DLC Phillips lime sludge there was no significant difference between these two. In any event, when the decrease in concentration is compared with the mother liquor in Tables 19 through 23, the concentration of major species in the 50th pore volume is consistently less under anaerobic leaching conditions than aerobic conditions. When the same comparison is made with trace elements, no clear trend is observed except for the case of lead. In every case, lead concentration in the 50th pore volume was significantly higher when leached under anaerobic conditions.

For an understanding of this behavior, it is necessary to observe that the pH of the aerobic leachate was acidic in all cases, whereas the anaerobic leachate was always basic. The increase in sulfate ion content in the aerobic leachate could have resulted from acid leaching of the sulfite ions that subsequently oxidized to sulfate. The increase in chloride ion in the aerobic leachate is believed to be a consequence of the release of chloride ion coprecipitated with the sulfite phase (30). The higher lead content in the anaerobic leachate is consistent with the observations noted previously where lead increased with increases in the pH of the system. It is believed that the lead behavior was a consequence of the relative stability of the basic lead carbonate in the system.

The acidic leachate of the aerobic columns was a consequence of atmospheric interaction with the leaching water that subsequently reacted with the sulfite phase to leach bisulfite from the sludge column. The leachate was then oxidized by exposure to the atmosphere producing sulfate and hydrogen ions. The pH of aerobic leachate for all sludges ranged between 4.5 and 6.0, depending on the initial alkalinity of the sludge; apparently, the unbuffered leaching solutions at pH 7 and 9 could not offset the stronger acid reactions.

Earlier mention was made of the independence of the concentration of major and trace species on the starting pH of the leaching waters. The exceptions were that, in the first sampled leachates, the sulfate content was slightly lower (approximately 10 percent) in the pH 9 column and the pH of the leachate of this column was always slightly higher than the pH 4 and 7 columns, which were identical. The other exception was in the concentration of lead, which was always higher in the initial sample for the pH 9 column. This behavior is in complete agreement with other observations which showed that the concentration of lead was higher in more basic waters.

Except for selenium in the anaerobic leachate of the TVA Shawnee limestone sludge and copper in the SCE Mohave aerobic leachate, only lead and zinc were consistently found at high concentrations (>0.1 mg/ℓ) in the initial leachate. In many cases, lead and zinc were found in the first pore volume at concentrations greater than that of the mother liquor. In the GM Parma sludge, all trace elements were found in the first pore volume at a concentration greater than the mother liquor. These elements were quickly flushed from the column and appeared thereafter at background levels.

When leaching behavior is compared in Figures 32 through 36, it appears that significant differences exist among the leaching results of major species. However, when this behavior is compared in Tables 19 through 23, certain similarities appear. Specifically, the sulfate concentration in the aerobic columns after 50 PVD reached a level of stability at values between 1100 and 1300 mg/ℓ, completely independent of the concentration of the mother liquor. Sulfate ion concentration in the 50th pore volume in the anaerobic columns showed a consistent 20 percent reduction in concentration, ranging between 900 and 1100 mg/ℓ. In the 50th pore volume, the chloride concentration was found to have stabilized in the range between 95 and 130 mg/ℓ in the aerobic columns and at about one half of this value in the anaerobic columns. The concentration of sulfate in the leachate was approximately that which is predicted from the solubility of gypsum. The concentration of chloride ion demonstrated a stability value that is not reconcilable with solubility theory and can only be understood if chloride ions are coprecipitated with both sulfite and sulfate phases.

9.2.5 *Pollution by Rainwater Leaching of Chemically Treated Wastes*

Several techniques or processes are available by which sludge may be treated by chemical additives to reduce its pollution potential and increase its environmental acceptability as a waste for disposal. The applications and costs of these processes or techniques are presented in Section X. In most cases, these processes convert the sludge to a more solidified state by various means, which may include secondary dewatering and cementitious reactions. When waste is converted to a solid, disposal management procedures are available to further reduce or eliminate the pollution potential. However, if these procedures are not employed, chemically treated sludge may be disposed of in a manner in which a chemical pollution potential exists. One such disposal technique is that in which free-standing rainwater is permitted to percolate through the waste. The resulting leachate will contain the chemical species in the waste that are free to move. These species can be salts from the mother liquor, chemical additives, soluble species from the solid waste, or chemical products resulting from waste reactions with the additives.

Leaching experiments were conducted for determination of the quality of leachate that could be expected from chemically treated FGD wastes. Both aerobic and anaerobic leaching conditions were experimentally conducted in the manner described in Section 9.2.4. In all cases, the chemically treated sludge was dried and pulverized before being packed into a leaching column, which procedure generated the maximum surface contact area for the flow of water through the treated sludge. This represents an operational case in which the cured material is fractured by heavy machinery during final placement.

The results of the leaching experiments are presented in Figures 40 through 46, in which only major species and trace elements at high concentrations are presented. These figures show leaching behavior similar to that observed in the leaching of untreated sludge. In most cases, the decrease in concentration of major species in the leachate took place within the first

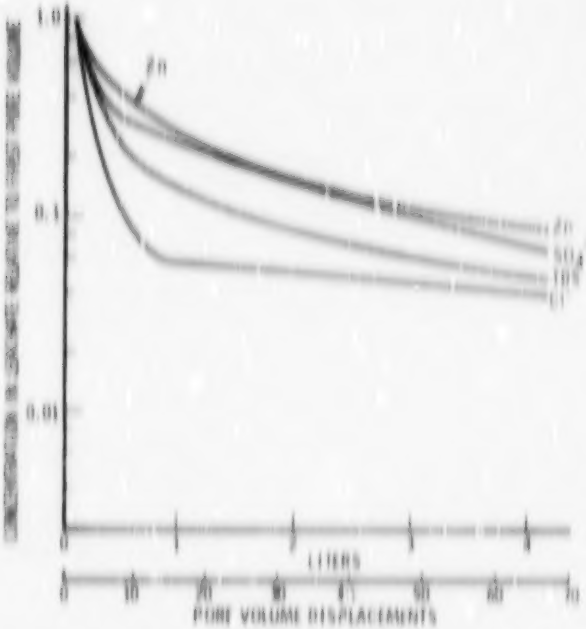

Figure 40. Analysis of leachate from TVA Shawnee (Chemfix) sludge: aerobic conditions.

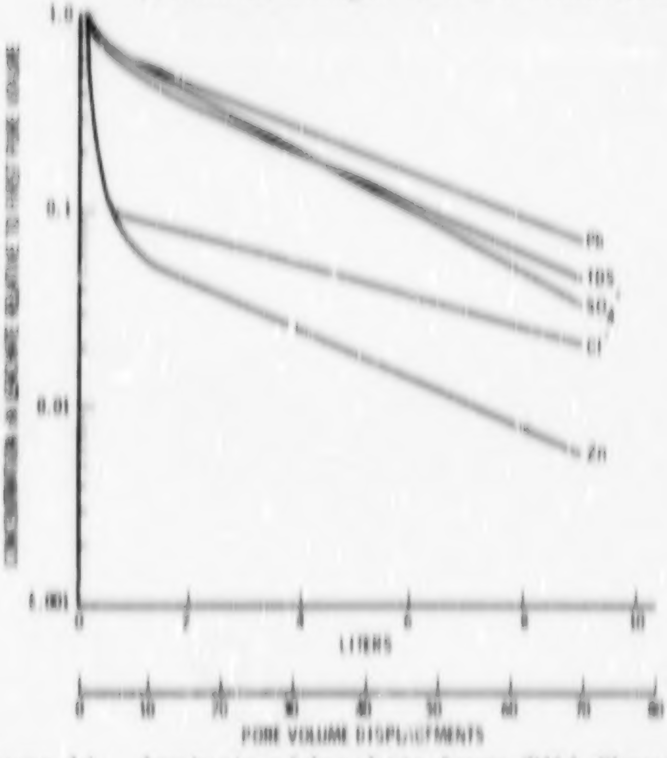

Figure 41. Analysis of leachate from TVA Shawnee (Chemfix) sludge: anaerobic conditions.

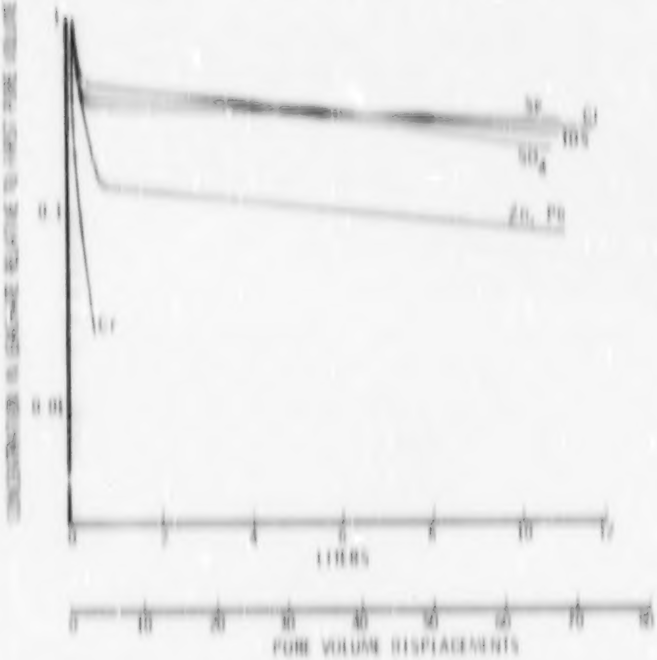

Figure 42. Analysis of leachate from TVA Shawnee limestone (IUCS) sludge: anaerobic conditions.

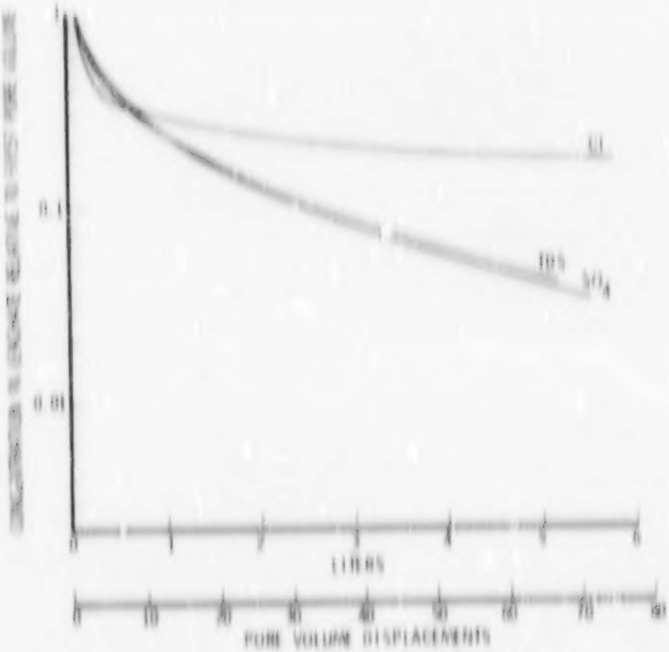

Figure 43. Analysis of Leachate from SCE Mohave (IUCS) sludge: aerobic conditions.

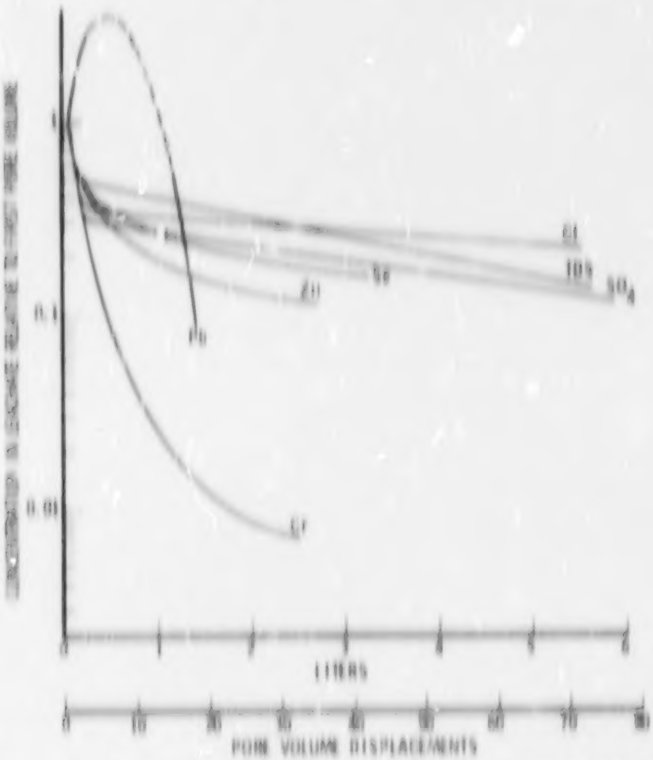

Figure 44. Analysis of leachate from SCE Mohave (IUCS) sludge: anaerobic conditions.

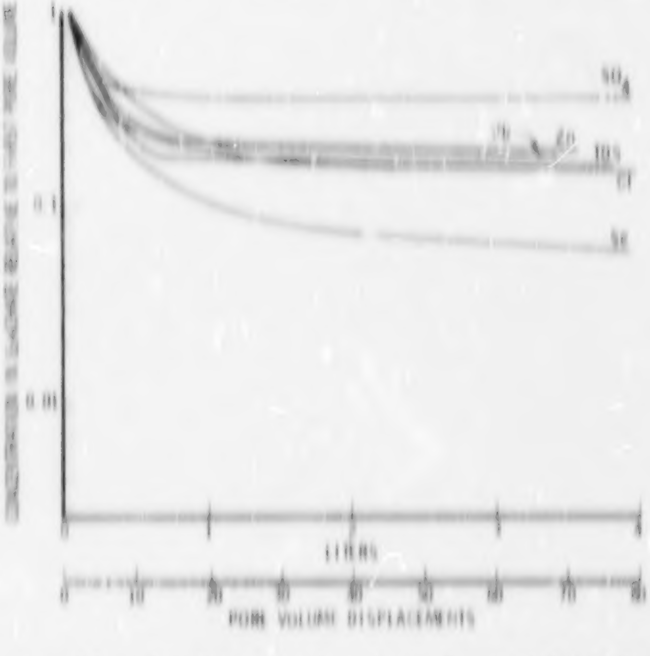

Figure 45. Analysis of leachate from DLC Phillips (Calcilox) sludge: aerobic conditions.

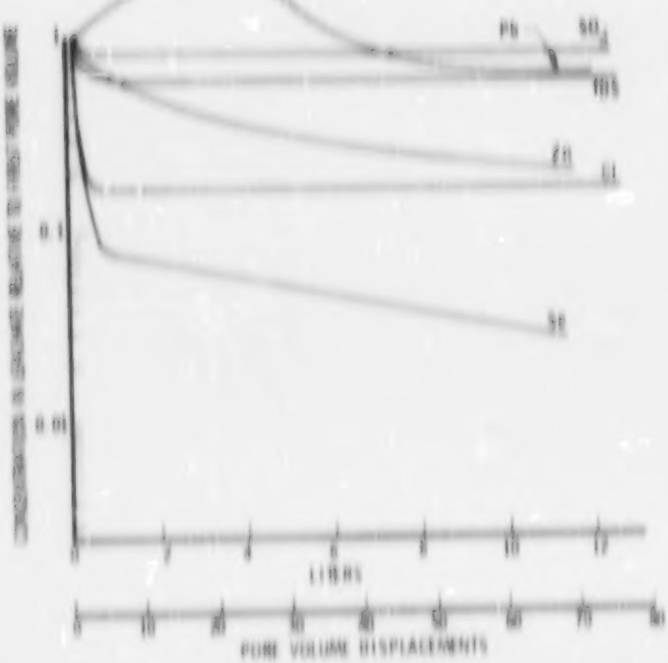

Figure 46. Analysis of leachate from DLC Phillips (Calcilox) sludge: anaerobic conditions.

few PVD. However, contrary to untreated sludge leaching, some major species did not leach in this way, but rather the decrease in concentration was more gradual. This was true even when a comparison was made with anaerobic leaching of untreated sludge. In the chemically treated sludge, no systematic trend was found in the decrease of the concentrations of major species when aerobic and anaerobic conditions were compared.

When the absolute concentrations for untreated materials (Tables 19 through 23) are compared with the values for treated materials (Tables 24 through 27) for the same scrubbing system and leaching conditions, it is observed that the concentration of major species in the first pore volume of the treated waste leachate is less than approximately 50 percent of the untreated sludge leachate. The relative decrease in concentration appears to depend on the sludge type, chemical treatment, and differences between aerobic and anaerobic leaching conditions.

A comparison of the trace element content of untreated sludge leachate and leachate from chemically treated sludge as given in either the figures or tables suggests that, in some cases, the origin of the trace elements was the chemical additive rather than the sludge. Specifically, the high initial concentration of chromium in the anaerobic leachate of both the TVA Shawnee limestone and SCE Mohave limestone sludge, chemically treated by I U Conversion Systems (IUCS), is particularly suggestive of an additive

TABLE 24. COMPARISON OF CHEMICAL CONSTITUENTS IN SLUDGE LIQUORS WITH LEACHATE AFTER 1 AND 50 PVD: TVA SHAWNEE LIMESTONE SLUDGE (CHEMFIX)

Constituent	Aerobic Conditions, mg/ℓ		Anaerobic Conditions, mg/ℓ	
	1st PVD	50th PVD	1st PVD	50th PVD
As	0.04	0.006	0.03	<0.003
Be	0.008	<0.001	--	--
Cd	0.003	<0.001	0.02	0.002
Cr	0.04	<0.001	0.08	<0.015
Cu	0.05	0.005	<0.01	<0.01
Pb	<0.035	<0.001	--	0.003
Hg	<0.005	<0.0005	0.0008	0.0004
Se	0.01	0.002	0.008	<0.005
Zn	0.5	0.065	1.25	0.015
Cl	1400	60	1200	40
F	0.9	0.2	1.1	0.6
SO_3	22	<0.1	42	7
SO_4	3000	250	2850	230
TDS	7000	500	5470	500
pH	4.70	6.01	6.93	9.26

TABLE 25. COMPARISON OF CHEMICAL CONSTITUENTS IN SLUDGE LIQUORS WITH LEACHATE AFTER 1 AND 50 PVD: TVA SHAWNEE LIMESTONE SLUDGE (UCS)

Constituent	Anaerobic Conditions, mg/ℓ[a]	
	1st PVD	50th PVD
As	<0.004	<0.004
Be	--	--
Cd	0.01	0.003
Cr	0.60	<0.01
Cu	0.04	<0.01
Pb	0.37	<0.03
Hg	0.0007	0.0002
Se	0.036	0.011
Zn	0.35	0.033
Cl	230	78
F	0.8	0.2
SO_3	34	22
SO_4	2700	980
TDS	5230	1500
pH	7.76	10.61

[a] The sample for aerobic conditions was inadequate.

TABLE 26. COMPARISON OF CHEMICAL CONSTITUENTS IN TREATED SLUDGE LEACHATE AFTER 1 AND 50 PVD; SCE MOHAVE LIMESTONE SLUDGE (IUCS)

Constituent	Aerobic Conditions, mg/ℓ		Anaerobic Conditions, mg/ℓ	
	1st PVD	50th PVD	1st PVD	50th PVD
As	0.02	<0.004	0.013	<0.004
Ba	0.011	0.003	--	--
Cd	0.02	<0.001	0.023	0.0013
Cr	0.08	0.003	1.8	<0.015
Cu	0.02	0.010	0.02	<0.01
Pb	0.07	0.033	0.13	0.03
Hg	<0.005	<0.00005	0.0003	<0.0005
Se	0.02	0.026	0.23	0.04
Zn	0.04	0.032	0.20	0.022
Cl	330	60	300	75
F	2.5	0.2	0.8	0.2
SO_3	1.5	0.5	34	17
SO_4	4000	200	4300	600
TDS	6800	400	5660	1100
pH	4.76	5.63	8.49	9.77

TABLE 27. COMPARISON OF CHEMICAL CONSTITUENTS IN TREATED SLUDGE LEACHATE AFTER 1 AND 50 PVD: DLC PHILLIPS LIME SLUDGE (CALCILOX BY DRAVO)

Constituent	Aerobic Conditions, mg/ℓ		Anaerobic Conditions, mg/ℓ	
	1st PVD	50th PVD	1st PVD	50th PVD
As	<0.01	<0.004	<0.01	<0.004
Be	0.006	<0.001	--	--
Cd	0.022	0.001	0.03	0.003
Cr	0.04	0.001	0.05	<0.015
Cu	0.03	0.01	0.02	<0.01
Pb	0.18	0.03	0.125	0.07
Hg	0.0007	<0.00005	0.001	0.0002
Se	0.15	0.01	0.146	0.005
Zn	0.16	0.03	0.16	0.037
Cl	600	95	600	90
F	2.6	0.6	5.5	1.7
SO_3	18	6	22	7
SO_4	1900	650	1925	1450
TDS	5600	900	3750	2150
pH	5.03	8.51	7.54	9.19

origin since the chromium content in the untreated sludge was high in either the sludge or the leachate. In a similar example, selenium appeared in the initial leachate from the DLC Phillips lime sludge, treated with the Dravo process, at a concentration of twice that found in the untreated sludge and at virtually identical concentrations in both aerobic and anaerobic leaching conditions.

On the other hand, lead and zinc appeared at relatively high concentrations in the initial leachate from the TVA Shawnee limestone sludge and again when this sludge was chemically treated, either by the IUCS or Chemfix process. Lead and zinc were also found in the leachate from the DLC Phillips lime sludge at relatively high concentrations and appeared again at approximately the same concentration levels in the leachate after chemical treatment by the Dravo process.

In the specific case of lead, it was observed that its concentration was always higher in the anaerobic leachate than the aerobic leachate of untreated sludges. This behavior was also present in the leachates from chemically fixed sludges.

It was previously observed that lead and zinc concentrations in the initial leachate from untreated sludge exceeded the concentration of these elements in the mother liquor. The same behavior was observed for the chemically treated sludges; in the chemically treated SCE Mohave limestone and DLC Phillips lime sludges, the lead concentration continued to rise for several PVD before receding to lower concentration levels.

In nearly all cases for major species, independent of their initial concentrations, the chemical species concentrations in the 50th PVD from chemically treated sludge was less than in the 50th PVD from untreated sludge. In the case of aerobic leaching conditions, the concentration was typically reduced to a value of 40 percent or less than that for untreated sludge. In the case of anaerobic leaching conditions, the concentration reduction was not as clearly revealed. In one case the concentration increased; in other cases the reduction was small, with the best case representing only a one-third reduction from the concentration of the untreated sludge.

The effect of chemical treatment of untreated sludge on the quality of leachate is generally an improvement in leachate quality dependent in part on the specific sludge and the specific chemical process. Generally, the concentration of specific major chemical species is one half or less in the leachate from the chemically treated sludge relative to the leachate from untreated sludge. In the case of aerobic leaching conditions, this relationship appears to hold for all leaching volumes; however, in anaerobic leaching, this reduction does not hold true at longer leaching times. In at least one case, the chemically treated sludge showed no improvement in leachate quality over untreated sludge.

When these data are examined for trace metals, it is seen that chemical treatment of sludge does not improve the leachate quality compared to the leachate of untreated sludge. In those cases in which high initial concentration of trace elements appeared in the leachate of untreated sludge, the same elements appeared when the sludge was chemically treated and responded identically under aerobic and anaerobic leaching conditions. In addition, the data suggest that the chemical additives used in the chemical processing may contribute trace elements to the leachate. Thus, chemical treatment by the methods evaluated would not be effective in alleviating the environmental pollution potential of trace elements. Other techniques, however, such as (a) reduction of concentration of major species, (b) reduction of permeability, and (c) superior disposal placement techniques made possible by chemical treatment can be effective if properly utilized.

9.3 ALTERNATIVE DISPOSAL TECHNIQUES

9.3.1 Ponding

The method of sludge disposal that represents the least deviation from state-of-the-art fly ash disposal is direct ponding into a disposal basin. In this method, the underflow of a clarifier is pumped to the pond where the solids settle. The supernate is returned to the scrubber because the soluble salt content is too high for effluent discharge. From the viscosity data and dewatering experiments, it is seen that in some sludges secondary dewatering can be conducted before pumping to the pond, while in other sludges the clarifier underflow has a water content close to the point at which secondary dewatering would prevent liquid transfer. In most sludges, the settled density is the lowest density of any dewatering method, and the sludge requires the largest disposal basin because of the large amount of water retained in the sludge. At the conclusion of filling the basin, the disposal site can either be maintained as a pond or allowed to dry, depending primarily upon the prevailing climatic conditions.

The environmental impact of pond disposal is strongly dependent upon the ability (a) to contain the components of a sludge so as to prevent environmental pollution and (b) to retire the disposal site in a manner that does not create a safety hazard or nuisance in subsequent land use. For pond disposal, the environment can be protected from chemical pollution, principally from leachate contamination of groundwater, by lining the pond basin with clay, impermeable soil cements, or synthetic materials. The need for liner materials is strongly suggested by the high permeability of the sludge (10 to 100 times greater than most indigenous soils) and the high concentration of chloride and sulfate ions in the leachate. However, if a liner material is not used, it is expected that not all trace elements will be attenuated by the subsoil. Additionally, soils do not significantly attenuate chloride or sulfate ions.

Pond retirement can be effected either by maintaining the pond as a lake or by allowing the sludge to dry and covering it with an overburden. In order to maintain the retired disposal basin as a lake, it is necessary to provide a balance between water loss and water input. The water loss may be by evaporation, and, in the case where no liner is used or a breach is developed in the liner, loss also occurs by percolation through the subsoil. Precipitation in excess of loss requires a means for eliminating excess water.

If precipitation is less than water loss, a means for maintaining water level must be used or the lake will eventually dry. If specific plans for overburden coverage are not made at the time of pond retirement, a dried lake will likely represent an environmental hazard or nuisance.

If a pond is retired by drying the sludge and covering it with an overburden, certain restrictions may limit reuse of the land. The overburden can be contoured so as to maximize runoff. If a liner is used, maximizing rainfall runoff and minimizing percolation of water through the overburden may be necessary to avoid resaturating the sludge. If no liner is used, proper contouring is necessary to minimize recharge to the water table and to minimize the pollution potential of the leachate from the sludge. In areas where the permeability of the subsoil is low, it is possible to prevent any contamination of the water table if the sludge leachate does not reach the water table during the time of active pond filling and, after drying and covering, if the subsequent disposal site is properly designed so that groundwater recharge is prevented. Under proper climatical, geological, and hydrological conditions, it is presumed possible to dispose of FGD sludge by ponding in an environmentally acceptable manner.

9.3.2 Ponding With Underdrainage

The method of disposal which includes underdrainage within a closed basin is a major variation of the ponding method of disposal. This method retains the advantage of transferring the sludge to the disposal site by liquid transfer, but, instead of supernate return to the scrubber, the leachate from the base of the sludge is returned to the scrubber. The advantages of this method are both economical and environmental. By avoiding a supernate head over the sludge, percolation of sludge leachate into the subsoil can be avoided during the active fill period. Upon retirement of the disposal site, the sludge is more easily dried and can be covered without regard for climatic conditions otherwise required for drying. Subsequent cover contouring is necessary for the reasons discussed in ponding, but the underdrainage system provides a means of sampling and elimination of leachate if required to prevent groundwater contamination. The primary economic advantage of this method is the elimination of the requirement for a disposal basin liner to prevent leachate percolation, except in those cases where the subsoil is highly permeable, and the relative ease of retirement.

The sludge that is allowed to drain packs to only a slightly higher density than settled sludge; thus, no savings in the size of the disposal basin can be gained. Also, limiting restrictions on subsequent land use are expected. Compaction techniques used with fly ash and other materials to increase density are shown not to be effective with FGD sludge, but compaction was shown to decrease permeability. Thus, while the underdrained sludge is physically amenable to compaction, it is not cost-effective for increasing density or strength, and it is detrimental to the free percolation of leachate through the sludge. Disposal by ponding with underdrainage offers added assurance of environmental acceptance over ponding, and in some cases it can be a more economical method of total disposal.

9.3.3 Dry Sludge Disposal

An alternative method of sludge disposal is that which uses a secondary dewatering method such as filtration or centrifugation, and the sludge cake is trucked to a disposal basin. From the dewatering experiments, it has been seen that, for most sludges tested, secondary dewatering does not remove a sufficient amount of water to gain structural stability from the sludge. Thus, a dry centrifuge or filter cake is not produced, and the resulting cake is not easily transported because of its thixotropic nature. However, the addition of fly ash, if available, can alleviate this problem. Since trucking is intrinsically more expensive than pumping, and because of the additional difficulties created by the thixotropic nature of the sludge (including rewetting), this method of disposal is attractive only in those cases where alternative methods are not possible.

The structural stability of sludge dewatered by filtration or centrifugation varies among the FGD sludges such that the restrictions that may be subsequently placed on land use must be determined on a case by case basis. The environmental acceptability of FGD sludge disposed of by this method will be highly dependent upon disposal site management techniques.

9.3.4 Chemically Treated Sludge Disposal

Several commercial processes are available by which FGD sludges are chemically treated to render them environmentally acceptable by several alternative disposal methods. An evaluation of three of these processes suggests that the soluble salt content in the leachate from treated sludge is typically one half or less than that of the untreated sludge. Additionally, the permeability of the treated sludge appears to be at least one order of magnitude less than that of the untreated sludge. Therefore, the expected dissolved salts that are leached from treated sludge and available to the environment are considerably less than from untreated sludge.

For every process examined, the structural stability of the treated sludge was far superior to that of the untreated sludge. The treated sludge texture ranged from soil-like, clay-like, to concrete-like and developed strength far in excess of natural soils. Restrictions on subsequent land use will depend upon local conditions and the long-time stability of the fixed sludge. Laboratory data have not been developed by any source from which it would be possible to predict the time-dependent stability of treated sludge.

Chemically treated sludges can be used as landfill in both submerged and above-grade conditions. In the submerged condition, the sludge serves as a lake bottom, and, if the sludge is sufficiently impermeable only a minimal leachate is available to the subsoil. In an above-grade condition, rainwater does not penetrate the "impermeable" surface, and a leachate is not produced. The environmental impact of treated sludge is less than that of untreated sludge under most disposal methods although the added assurance afforded by the chemical process increases the cost of disposal. The cost effectiveness of chemical treatment must be evaluated in the context of specific land use limitations and disposal site restrictions that exist as unique conditions at each power plant facility.

In the absence of federal regulations for FGD sludge disposal, there is no evidence that untreated sludge disposal cannot be environmentally acceptable with proper placement and management. Conversely, chemical treatment without regard to proper placement and management is not likely to assure environmental acceptance. Furthermore, a properly placed and managed untreated FGD disposal site is more likely to meet environmental acceptance criteria than a poorly managed disposal site for treated FGD wastes.

9.4 ASSESSMENT OF THE CHEMICAL POLLUTION POTENTIAL ON THE ENVIRONMENT BY ALTERNATIVE DISPOSAL METHODS

Pollution of groundwater by the action of rainwater percolating through FGD sludge is a genuine concern in the disposal of this material. Laboratory experimentation has shown that relatively high concentrations of dissolved chemical species in the liquor from untreated sludges persist in the leachate until at least five PVD have passed through the sludge. Thereafter, the concentration depends on the solubility of the chemical phases in the sludge solids. The rate at which rainwater passes through FGD wastes has been measured in the range of 10^{-4} cm/sec, equivalent to soils of silty sand. The pollution of groundwater, determined by mass loading (mass/unit area) is calculated from the amount of pollutant that is carried by the leaching water to the groundwater.

The potential pollution that is possible from sludge when treated by any of several processors can be reduced by several orders of magnitude. Such an improvement has resulted from the (a) reduction of available chemical species (lower solubility) in the treated sludge, (b) reduction of standing rainwater by promoting runoff, and (c) reduction in the rate of water permeation through chemically treated material (lower permeability). In nearly every case, the eventual pollutant concentration of the leachate was less than one-half that of the leachate from untreated sludge under similar conditions of FGD waste placement and disposal site management. Additionally, the runoff from treated waste can be more easily maximized, making less than one tenth of the rainfall available for seepage. Since the permeation coefficient of treated waste is typically reduced by at least an order of magnitude, the mass loading per year to the groundwater may be reduced by a factor of 10 to 10,000. Thus, the real pollution measured by mass loading can be reduced by large amounts.

The consequence of much lower permeability rates of chemically treated sludge is that many years will pass before five PVD in the sludge will reduce the leachate concentration to the level of the soluble salts. Therefore, while the pollution of groundwater by untreated sludge can be severe for a short period of time and low thereafter, the pollution input caused by chemically treated sludge, at any given time, is never severe but will be sustained for much longer periods of time. The latter case is more consonant with nature, which weathers natural deposits slowly but constantly. However, since the high concentration of the leachate is not quickly flushed from treated

FGD wastes, the potential exists that a later unexpected event could result in the release of soluble chemical constituents with the possible consequence of environmental pollution. Such an event might be the result of a subsequent land use which requires extensive digging into the FGD sludge. Therefore, long term land-use planning will be necessary.

An evaluation of the amount of chemical pollutants that are available to the environment by leaching can be determined from the results of the leaching data summarized in Figure 47 and the permeability data summarized in Figure 17. An evaluation was made for an FGD waste containing 6000 mg/ℓ dissolved solids in the mother liquor and disposed of by each of the alternative techniques discussed in Section 9.3. The evaluation was made on the assumption that the leachate quality would respond according to the presentation in Figure 47 and that the rate of passage of the leachate through the sludge would be 10^{-4} cm/sec for untreated sludge and 10^{-5} cm/sec for treated sludge. The waste was placed to a depth of 30 ft during a five-year fill period. In the cases where the method of disposal was undrained ponding, it was assumed that a maximum hydraulic head of 6 ft was used during filling and a 1-ft head, thereafter, when retired as a lake.

The results of this evaluation are presented in Figure 48 for cases described in Table 28. Cases 1 and 2 represent the ponding technique of disposal in which the final disposition of the pond is a lake. Case 1 is for untreated FGD waste, and Case 2 is for treated waste. Cases 3 and 4 represent pond disposal of untreated and treated waste, respectively, in which supernate is not allowed on the surface of the pond during filling and the disposal site is retired by grading with the landscape. In these cases, the

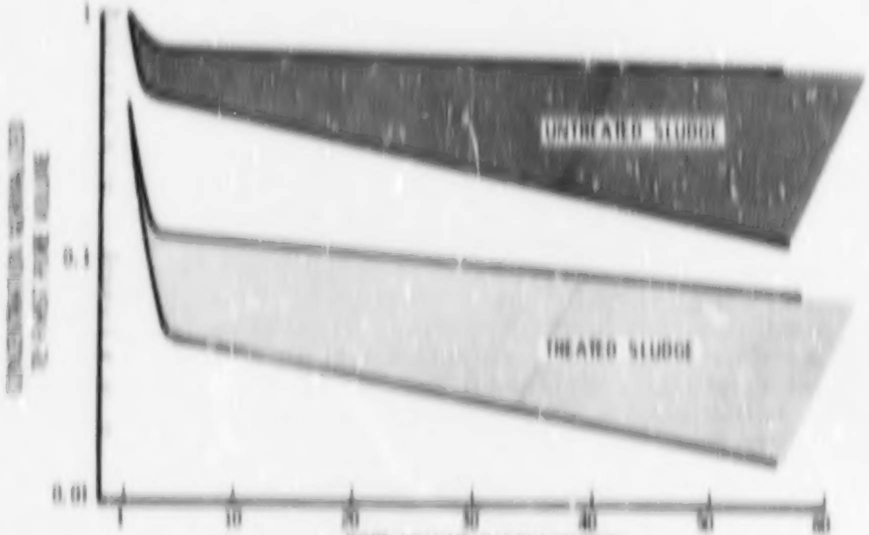

Figure 47. Leachate TDS from treated and untreated sludges as a function of PVD.

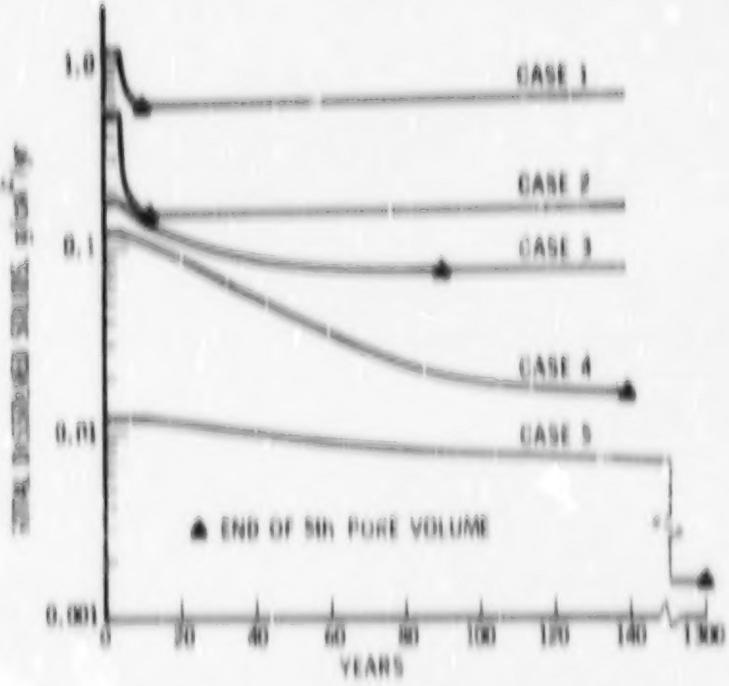

Figure 48. Mass loading of TDS to subsoil for various disposal modes of treated and untreated FGD wastes.

amount of water recharged to the basin represents a normal recharge for indigenous soil. Case 5 is the condition in which treated FGD waste is disposed of in a managed landfill where only 10 percent of the normal recharge is allowed to penetrate the waste because runoff has been maximized. Figure 48 plots the TDS that are expected to reach the disposal site subsoil per year as a function of time. Also plotted on each curve is an indication of the point in time at which the flushing action of the leachate reaches five PVD.

This evaluation shows that, depending on the disposal method selected, the mass loading of pollutants to the groundwater can be reduced by as much as two orders of magnitude. Moreover, the significance of disposal site management as a means of preventing chemical pollution to the environment is clearly shown. Although chemical treatment reduced the pollutant load under each condition considered, the larger reduction in pollution load was a consequence of minimizing rainwater recharge to the subsoil of the disposal basin. This evaluation places in perspective the value of chemical treatment and site management with respect to the environmental acceptability of FGD waste disposal.

TABLE 28. INPUT DATA FOR STUDY CASES

Case	Disposal Method	Surface Water	FGC Waste 5-Year Fill			
			Waste Condition	Depth, ft	Permeability, cm/sec[b]	Fractional Pore Volume
1	Lake[a]	Constant supernate	Untreated	30	10^{-4}	0.67
2	Lake[a]	Constant supernate	Treated	30	10^{-5}	0.67
3	Pond	10. in./yr recharge	Untreated	30	10^{-4}	0.67
4	Pond	10. in./yr recharge	Treated	30	10^{-5}	0.67
5	Landfill	1 in./yr recharge	Treated	30	10^{-5}	0.67

[a] Assumed maximum hydraulic head of 6 ft during filling, including depth of wastes; 1 ft constant water cover thereafter.

[b] For all cases, subsoil permeability = 10^{-5} cm/sec.

SECTION X

DISPOSAL APPLICATIONS AND ESTIMATED COSTS

Alternatives available for the disposal of flue gas desulfurization (FGD) wastes comprise several different approaches to ponding and landfilling, each having distinct characteristics as to complexity, cost, pollution potential, land requirements, land reclamation, and degree of technical development. Additionally, the type of disposal selected for a given site may be dictated or influenced by local conditions such as distance to disposal site, topography, weather, soil characteristics, depth of water table, and ground water characteristics. Considerable discussion of the methods available and already selected has been presented by The Aerospace Corporation (1-10), Haas and White (31), Crowe (32), PEDCo-Environmental Specialists, Inc. (33), U.S. Environmental Protection Agency (34), U.S. Army Engineer Waterways Experiment Station (35), and others.

In this section, a general review of disposal methods is given. The methods selected by power utilities that have scrubbers which are operational or were to be operational in 1976 are identified, and a disposal cost summary is given. The EPA field disposal evaluation project at the TVA Shawnee station (2) and the status, through 1979, of utility power plant fixation disposal commitments are reported in separate documents. These studies are continuing, and a general summary of all FGD waste disposal will be provided in an Aerospace report to the EPA later in 1977.

10.1 DISPOSAL METHODS

Environmentally sound disposal methods, regardless of the type used, must provide the means of preventing or minimizing the seepage of waste liquors to water supplies. These are grouped into two general categories: (a) ponding of untreated waste and (b) landfilling with chemically treated or physically conditioned waste. Each method has unique characteristics, and one or more may be applicable at a given site, depending on site conditions and the overall objectives of the user. The approaches that are in use or that show good potential are listed in Table 29, with significant comparative factors indicated for each approach. Methods 1 through 4, which cover ponding and chemical treatment ("fixation"), have been or are being used or evaluated in the field; methods 5 and 6, landfilling with untreated wastes, are being evaluated at the EPA Shawnee field evaluation project. Also, a tabulation of SO_2 scrubber waste disposal systems that are operating or that were planned to be operating in 1976 is given in Table 30, with much of

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TABLE [illegible]. SIGNIFICANT FEATURES OF DISPOSAL METHODS

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		X	X	X		X			X			
[illegible]					X	X			X	X		X
[illegible]	X							X	X	X	X	X
[illegible]	X						X			X	X[b]	X
[illegible]	X						X			X	X[b]	X
[illegible]		X	X	X		X				X		X

[a] [illegible]

[b] [illegible]

TABLE 30. FGD DISPOSAL SYSTEMS OPERATING BY END OF 1975

Utility Company and Station	New or Retrofit	Size of FGD Unit, MW equiv.	Absorbent	Startup Date	FGD Waste Treatment Process or Processor	Disposal Method
Arizona Public Service, Cholla, No. 1	Retrofit	115	Limestone	10/73	None	Pond
General Motors, Chevrolet Parma, Nos. 1, 2, 3, and 4	Retrofit	32	Double alkali	3/74	None	Haul to landfill
Gulf Power Co., Scholz, No. 1A	Retrofit	20	Double alkali	2/75	None	Lined pond
Kansas City Power and Light, Hawthorn, No. 3	Retrofit	[illegible]	Limestone injection and wet scrub	11/72	None	Pond
Kansas City Power and Light, Hawthorn, No. 4	Retrofit	100	Limestone injection and wet scrub	8/72	None	Pond
Kansas City Power and Light, La Cygne, No. 1	New	820	Limestone	2/73	None	Pond
Kansas Power and Light, Lawrence, No. 4	Retrofit	125	Limestone injection and wet scrub	12/68	None	Pond
Kansas Power and Light	New	400	Limestone injection and wet scrub	11/71	None	Pond
Kentucky Utilities, Green River, Units 1 and 2	Retrofit	64	Lime	9/75	None	Pond

TABLE 30. FGD DISPOSAL SYSTEMS OPERATING BY END OF 1976 (Continued)

Utility Company Power Station	New or Retrofit	Size of FGD Unit, MW equiv.	Absorbent	Startup Date	FGD Waste Treatment Process or Processor	Disposal Method
Key West Utility Board, Stock Island Plant	New	37	Limestone	10/72	None	Pond
Montana Power Co., Colstrip, No. 1	New	360	Lime	10/75	None	Pond
Nevada Power, Reid Gardner, No. 1	Retrofit	125	Sodium carbonate	4/74	None	Pond
Nevada Power, Reid Gardner, No. 2	Retrofit	125	Sodium carbonate	[illegible]	None	Pond
Public Service Co. of Colorado, Valmont, No. 5	Retrofit	[illegible]	Limestone	10/74	None	Pond
Montana Power, Colstrip, No. 2	New	360	Lime	7/76	None	
Nevada Power, Reid Gardner, No. 3	New	125	Sodium carbonate	6/76	None	
[illegible], Sherburne, No. 1	New	[illegible]	Limestone	[illegible]	None	Pond
Rickenbacker AFB, Rickenbacker	Retrofit	20	Lime	3/76	None	
Springfield City Utilities, Southwest, No. 1	New	200	Limestone	[illegible]	None	
Arizona Public Service, Four Corners, No. 5A	Retrofit	160	Lime	2/76	None	

TABLE 30. FGD DISPOSAL SYSTEMS OPERATING BY END OF 1976 (Continued)

Utility Company Power Station	New or Retrofit	Size of FGD Unit, MW equiv.	Absorbent	Startup Date	FGD Waste Treatment Process or Processor	Disposal Method
Central Ill. Light Co., Duck Creek, No. 1	New	100		6/76	None	
Detroit Edison, St. Clair, No. 6	Retrofit	180	Limestone	1/76	None	Pond
Commonwealth Edison, Will County, No. 1	Retrofit	167	Limestone	2/72	Lime and fly ash (Dravo, alternatives)	Planned landfill
Duquesne Light Co., Phillips	Retrofit	387	Lime	7/73	Dravo ponding	Haul to landfill
Duquesne Light Co., Elrama	Retrofit	510	Lime	10/75	IU Conversion Systems	Lined landfill
Gulf Power Co., Scholz, Nos. 1B and 2B	Retrofit	23		2/75	Chiyoda gypsum	Lined pond
Columbus and Southern Ohio Electric, Conesville, No. 5	New	400	Lime	6/76	IU Conversion Systems	Lined landfill
Louisville Gas and Electric, Cane Run, No. 4	Retrofit	178	Lime	6/76	None	
Pennsylvania Power Co., Bruce Mansfield, No. 1	New	825	Lime	4/76	Calcilox (Dravo)	Dam and lake
Texas Utilities Co., Martin Lake, No. 1	New	793	Limestone	9/76	Fixation (Research Cottrell)	Landfill
Louisville Gas and Electric, Paddys Run, No. 6	Retrofit	65	Lime	4/73	Compacted with fly ash	Borrow pit

the data based on information provided by PEDCo (33). These projects are referred to as "current disposal systems" in this discussion. Of these, 21 units are using ponding, and 8 are using fixation or physical conditioning, with a total capacity of 4338 and 2983 MW, respectively. Commitments to 1983 (3, 33, 19) identify approximately 80 units committed to nonregenerable scrubbers (~ 32,000-MW capacity), of which 15 units (7155-MW capacity) are commited to chemical treatment of FGD wastes.

Each of the methods listed in Table 29 offers a different form of protection against water pollution and a different approach to land reclamation. Since the long-term effects of ponding and landfilling are still being evaluated, no single method is considered superior for all cases. Table 31 summarizes the most significant factors associated with each form of disposal.

10.2 DISPOSAL COST ESTIMATES

Cost estimates for ponding and chemical treatment (fixation) plus landfilling have been made and reported by Aerospace on several occasions. In recent studies, performed during the task of coordinating the EPA field disposal evaluation at the TVA Shawnee station, detailed cost estimates were made of fixation and disposal and were reported (3). The ponding cost estimates presented in (1) and (5) are updated in Section 10.2.1 and are compared with a summary of the fixation disposal costs in Section 10.2.2.

10.2.1 Ponding Cost Estimates

Disposal pond costs are dependent on construction and equipment factors such as dike construction, ancillary equipment, liner materials and installation, and land costs, as well as factors which are a function of geographic location such as shipping and labor. An analysis of these factors was made by Aerospace (1) in 1973 and was subsequently revised (2) in November 1974 to reflect sharp price increases during that period for flexible liner materials, equipment, and construction. Since that time, additional work has been published (3 - 4), which correlates well with the earlier work. Since 1974 the price changes have been more moderate, and in this report we have updated the earlier estimates using economic indices as of 1 January 1976 (5).

The estimates are based on a 1000-MW power plant burning coal with 3 percent sulfur and 12 percent ash. The service life of the power plant is assumed to be 30 years, operating at an average load factor of 50 percent, with an annual average sludge (50 percent solids, including ash) production of 930,000 metric tons (1,025,000 short tons). The annualized costs include the costs for labor, maintenance, and capital charges of 18 percent. The annualized costs include the costs for labor, maintenance, and capital charges of 18 percent. The capital charges include replacements, insurance, taxes, cost of capital based on 50/50 debt-equity funding, and the use of straight-line depreciation.

TABLE 31. SIGNIFICANT ENVIRONMENTAL FACTORS ASSOCIATED WITH ALTERNATIVE WASTE DISPOSAL METHODS

Disposal Method	Land Reclaimable	Leachate Concentrations Meet Drinking Water Criteria	Leachable Constituents	Lining and/or Underdrain	Long-Term Pollution Control
Ponding	No	No	Large	Yes	Questionable
Chemical Treatment Landfill	Yes	No	Minimal	No[a]	Good Potential
Untreated Landfill[b]	Yes	No	Large	Yes	Good Potential[c]

[a] For extreme cases, e.g., highly porous soil, lining or underdrainage may be appropriate.

[b] This method has little or no controlled field evaluation but will be evaluated by EPA (2).

[c] Lining or underdrainage and impermeable cap after completion offer good potential for long-term control.

Figure 49 presents a summary of the typical installed costs of various liner materials. The range of costs shown reflect variations in the cost of materials, transportation, labor, and supplier discount practices. Two of these materials, 20-mil polyvinyl chloride (PVC) and 30-mil Hypalon, are considered to be representative of the spread in practical liner costs, and each was used in estimating 30-year average disposal costs. The results, shown in Figures 50 and 51 are presented for waste depths varying from 10 to 40 ft. These costs were estimated for a total of three ponds, each having a 10-year sludge capacity. Also, it was assumed that all of the land needed for the 30-year output would be purchased at the beginning of the project. Equipment costs were included for pumps and a two-way pipeline of 1.6 km (1 mi.), instrumentation to monitor effluent to the pond, and instrumentation to measure soil resistivity as a means of detecting leaks in the pond linear. Total labor costs were included at an annual rate of $102,000. It was also assumed that decreasing quantities of land would be needed over the 30-year operating period as a result of both the diminishing quantities of sludge being produced and savings realized in the joint use of dike walls by multiple ponds. Land costs were estimated to vary between $1000/acre and $5000/acre. The results show that disposal costs, including land at $1000/acre, for 50 percent solids, are about $2.85/ton for PVC and $3.90/ton for Hypalon at a waste depth of 30 ft. (These values increase to $3.50 and $4.30/ton, respectively, when a land cost of $5000/acre is used.) Ponding costs are converted to a dry FGD waste basis and compared with fixation disposal costs in Table 7. The total capital investment and annual operating costs for both PVC-20 and Hypalon-30 are given in Tables 32 through 37.

10.2.2 Cost Comparisons: Ponding Versus Fixation

A comparison of the ponding cost estimates developed in Section 10.2.1 and the fixation disposal cost estimates presented in (2) is shown in Table 7. These costs are given in units of dollars per ton of waste (dry), dollars per ton of coal, and mills per kilowatt hour. This comparison indicates that the cost of ponding with liner installed is approximately 75 percent of the fixation disposal costs or 40 percent if the pond has a natural clay liner. Excluded from these values are additional costs for the reclamation of the site, which may include the addition of top soil and nutrients on fixed landfills, and a yet-to-be-defined procedure for closing down a pond for permanent environmental protection. Also excluded is any cost reduction in terms of realizing the residual value of the land where applicable and any benefit to be realized from including current ash disposal with FGD total waste disposal where applicable.

Background information for these cost estimates is given in Tables 32 through 37 which provide capital costs for ponding at 1,000 MW station. Values consider cost variations of liner materials and land, and are given for three different dike heights. Also given is the conversion of capital costs to annual operating costs in dollars per ton of wet sludge (50 percent solids) for a 30-year lifetime.

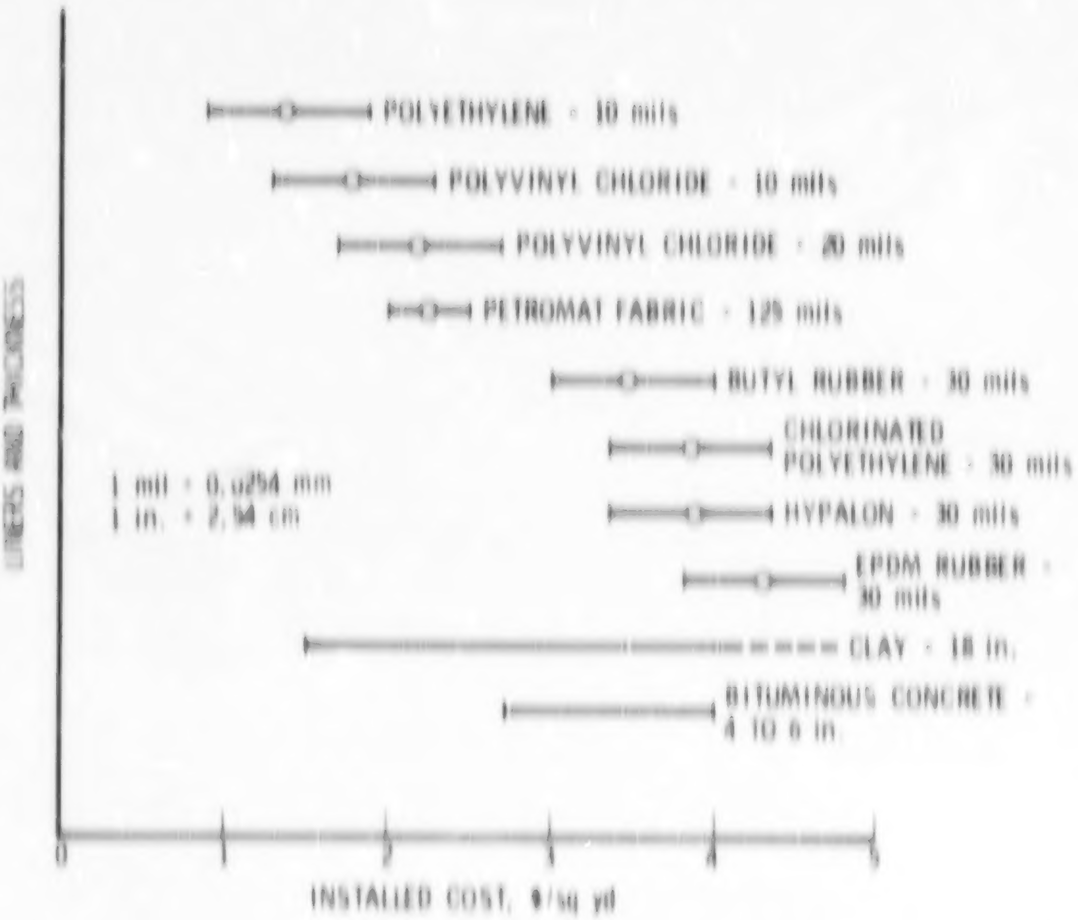

Figure 49. Installed liner costs.

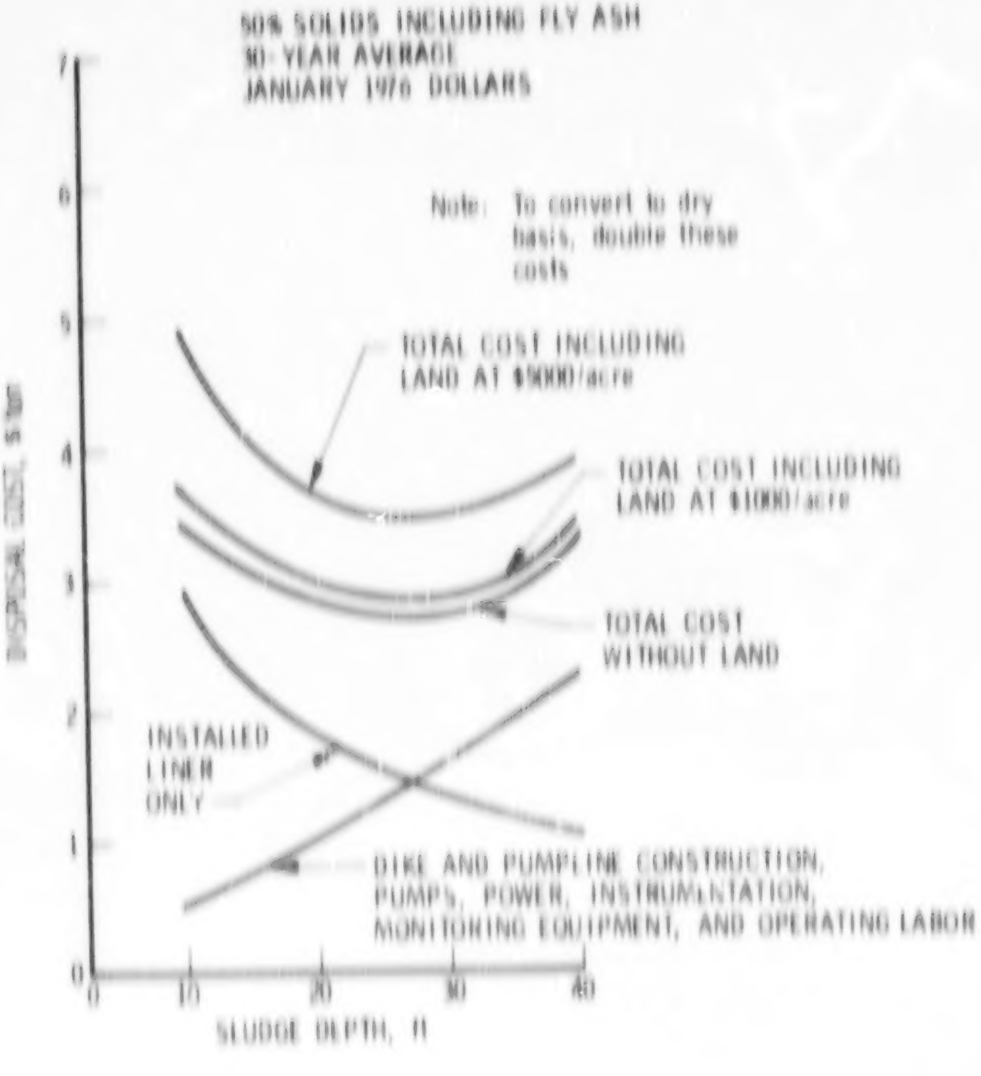

Figure 50. FGD waste ponding disposal costs: 20-mil PVC.

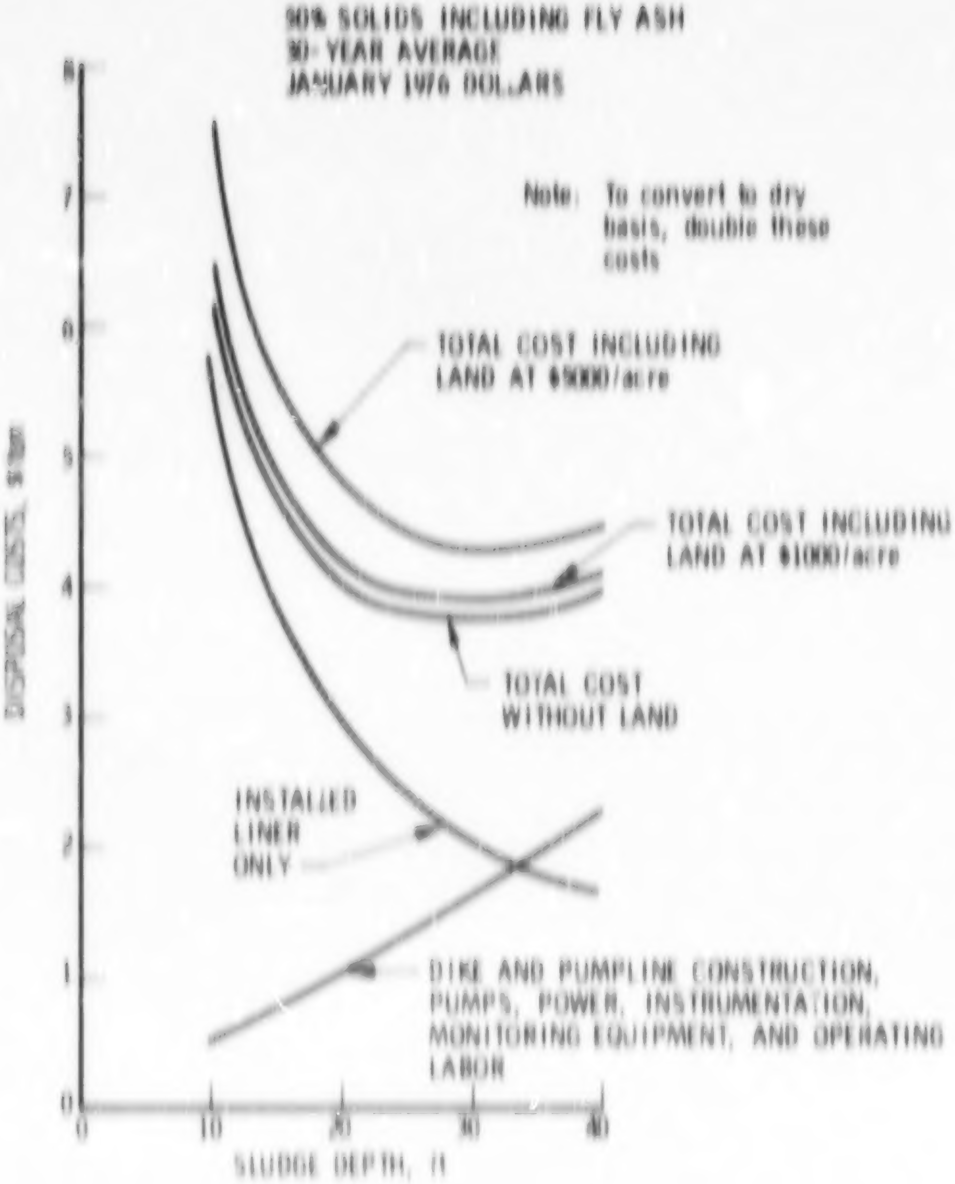

Figure 51. FGD waste ponding disposal costs: 10-mil Hypalon.

TABLE 32. TOTAL PONDING COSTS: PVC-20 LINER; 10-FT SLUDGE DEPTH (JANUARY 1976 DOLLARS; 1000-MW PLANT)[a]

Total Investment, $ Millions

Installed Liner = 16.5

Construction[b] = 2.4

Liner + Construction[b] + $1000/acre Land = 20.56

Liner + Construction[b] + $5000/acre Land = 27.20

Annual Operating Costs

Cost Item	Total Cost, $ Millions		Cost/Wet Ton, $[c]	
Liner	2.97		2.90	
Construction/Equipment[b]	0.43		0.42	
Operating Labor	0.102		0.10	
Subtotal	3.502		3.42	
$1000/acre Land	0.300		0.29	
$5000/acre Land		1.49		1.45
Total	3.802	4.992	3.71	4.87

[a] Based on disposal of 1.025×10^6 wet tons/year, 50 percent solids, 30-year average.

[b] Construction includes dike construction, pipeline, pumps, operating power, instrumentation, and monitoring equipment.

[c] Multiply by 2 to convert to $/ton (dry).

TABLE 33. TOTAL PONDING COSTS: PVC-20 LINER; 30-FT SLUDGE DEPTH (JANUARY 1976 DOLLARS; 1000-MW PLANT)[a]

Total Investment, $ Millions

Installed Liner = 10.05
Construction[b] = 5.36
Liner + Construction[b] + $1000/acre Land = 16.346
Liner + Construction[b] + $5000/acre Land = 20.05

Annual Operating Costs

Cost Item	Total Cost, $ Millions		Cost/Wet Ton, $[c]	
Liner	1.81		1.77	
Construction/Equipment[b]	0.97		0.94	
Operating Labor	0.102		0.10	
Subtotal	2.882		2.81	
$1000/acre Land	0.168		0.16	
$5000/acre Land		0.842		0.82
Total	3.050	3.724	2.97	3.63

[a] Based on disposal of 1.025 x 10^6 wet tons/year, 50 percent solids, 30-year average.

[b] Construction includes dike construction, pipeline, pumps, operating power, instrumentation, and monitoring equipment.

[c] Multiply by 2 to convert $/ton (dry).

TABLE 34. TOTAL PONDING COSTS: PVC-20 LINER; 40-FT SLUDGE DEPTH (JANUARY 1976 DOLLARS; 1000-MW PLANT)[a]

Total Investment, $ Millions
Installed Liner = 5.92
Construction[b] = 12.26
Liner + Construction[b] + $1000/acre Land = 18.788
Liner + Construction[b] + $5000/acre Land = 21.220

Annual Operating Costs

Cost Item	Total Cost, $ Millions		Cost/Wet Ton, $[c]	
Liner	1.07		1.04	
Construction/Equipment[b]	2.21		2.16	
Operating Labor	0.102		0.10	
Subtotal	3.382		3.30	
$1000/acre Land	0.109		0.11	
$5000/acre Land		0.547		0.53
Total	3.491	3.929	3.41	3.83

[a] Based on disposal of 1.025×10^6 wet tons/year, 50 percent solids, 30-year average.

[b] Construction includes dike construction, pipeline, pumps, operating power, instrumentation, and monitoring equipment.

[c] Multiply by 2 to convert to $/ton (dry).

TABLE 35. TOTAL PONDING COSTS: HYPALON-30 LINER; 10-FT SLUDGE DEPTH (JANUARY 1976 DOLLARS; 1000-MW PLANT)[a]

Total Investment, $ Millions

Installed Liner = 31.93

Construction[b] = 2.4

Liner + Construction[b] + $1000/acre Land = 35.59

Liner + Construction[b] + $5000/acre Land = 42.63

Annual Operating Costs

Cost Item	Total Cost, $ Millions		Cost/Wet Ton, $[c]	
Liner	5.75		5.61	
Construction/Equipment[b]	0.432		0.42	
Operating Labor	0.102		0.10	
Subtotal	6.284		6.13	
$1000/acre Land	0.300		0.29	
$5000/acre Land		1.49		1.45
Total	6.584	7.774	6.42	7.58

[a] Based on disposal of 1.025 × 10^6 wet tons/year, 50 percent solids, 30-year average.

[b] Construction includes dike construction, pipeline, pumps, operating power, instrumentation, and monitoring equipment.

[c] Multiply by 2 to convert to $/ton (dry).

TABLE 36. TOTAL PONDING COSTS: HYPALON-30 LINER; 25-FT SLUDGE DEPTH (JANUARY 1976 DOLLARS; 1000-MW PLANT)[a]

Total Investment, $ Millions

Installed Liner = 16.63

Construction[b] = 5.36

Liner + Construction[b] + $1000/acre Land = 22.926

Liner + Construction[b] + $5000/acre Land = 26.670

Annual Operating Costs

Cost Item	Total Cost, $ Millions		Cost/Wet Ton, $[c]	
Liner	2.99		2.92	
Construction/Equipment[b]	0.965		0.94	
Operating Labor	0.102		0.10	
Subtotal	4.057		3.96	
$1000/acre Land	0.168		0.16	
$5000/acre Land		0.842		0.82
Total	4.225	4.899	4.12	4.78

[a] Based on disposal of 1.025×10^6 wet tons/year, 50 percent solids, 30-year average.

[b] Construction includes dike construction, pipeline, pumps, operating power, instrumentation, and monitoring equipment.

[c] Multiply by 2 to convert to $/ton (dry).

TABLE 57. TOTAL PONDING COSTS: HYPALON-30 LINER; 40-FT SLUDGE DEPTH (JANUARY 1976 DOLLARS; 1000-MW PLANT)[a]

Total Investment, $ Millions

Installed Liner = 9.62

Construction[b] = 12.26

Liner + Construction[b] + $1000/acre Land = 22.49

Liner + Construction[b] + $5000/acre Land = 24.92

Annual Operating Costs

Cost Item	Total Cost, $ Millions		Cost/Wet Ton, $[c]	
Liner	1.732		1.69	
Construction/Equipment[b]	2.210		2.16	
Operating Labor	0.102		0.10	
Subtotal	4.044		3.95	
$1000/acre Land	0.109		0.11	
$5000/acre Land		0.547		0.53
Total	4.153	4.591	4.06	4.48

[a] Based on disposal of 1.025×10^6 wet tons/year, 50 percent solids, 30-year average.

[b] Construction includes dike construction, pipeline, pumps, operating power, instrumentation, and monitoring equipment.

[c] Multiply by 2 to convert to $/ton (dry).

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APPENDIX A

CHARACTERIZATION OF SLUDGE SOLIDS

The characterization of the solids portion of flue gas desulfurization (FGD) sludges included the identification of the separate crystalline phases; determination of the amount of each of these phases; and delineaton of the morphological traits of these phases relative to particle size, shape, and distribution. The crystalline phase identification was done by x-ray diffractometry by standard methods and provided a knowledge of the crystal structures and the relative amount of each structure within each sample material. The amount of each phase was determined by chemical analysis of the solid portion of each sludge by the techniques described in Appendix C. Reconstitution of phases was accomplished not only from the chemical analyses but also from the determination of the chemistry of the soluble and hydrous forms of the solids portion and from the evaluation of the relative quantities indicated by the x-ray analyses.

The physical characteristics of the individual particles were determined through observation by scanning electron micrography. These observations revealed the shape and growth habits of the crystalline phases, the particle sizes and distribution, and the presence (or absence) of phases indicated by either x-ray or chemical analyses.

A.1 X-RAY DIFFRACTION CHARACTERIZATION

The objective in the use of x-ray diffraction techniques on power plant FGD waste was to provide quantitative characterization of the crystalline phases in the solid waste. The results of the study indicated that, although this method is not suitable for quantitative analyses, it is useful for phase identification that can not be performed by other techniques.

Sludges were oven-dried at temperatures between 70° and 80° C, and the resultant dry powders were mounted in a conventional powder sample mount for x-ray diffraction. Copper radiation at 50 kV, a nickel filter, and a scintillation counter were used. Diffraction peaks between 10- and 50-deg Bragg angle were recorded, and the resulting patterns were interpreted. The results of these analyses are presented in Table A-1. The relative intensity values refer only to the intensity among phases in each specific sludge and indicate no relationship between sludges. Furthermore, since no standards were used, relative intensities do not necessarily infer relative concentration of the various phases within a sample because of the differences in diffraction behavior among differing crystalline phases.

TABLE A-1. RELATIVE X-RAY INTENSITIES OF CRYSTALLINE PHASES IN DRIED SLUDGE SAMPLES

[illegible]	TVA Shawnee [illegible]	TVA Shawnee [illegible]	TVA Shawnee [illegible]	TVA Shawnee [illegible]	SCE Mohave [illegible]	GM Parma Double Alkali [illegible]	APS Cholla [illegible]	DLL Phillips [illegible]	CPL Gadsby Double Alkali [illegible]
Gypsum [illegible]	Strong	Strong	Very Strong	Trace	Strong		Strong	Strong	Weak
Calcium Sulfite Hemihydrate [illegible]	Moderate	Moderate	Strong	Strong	Trace	[illegible]	Trace	Moderate	
Calcium Sulfate Hemihydrate [illegible]					Very Weak	Strong			Strong
Anhydrite [illegible]									Trace
Calcite [illegible]	Moderate	Very Weak	Weak		Moderate	Weak			Weak

[illegible]

The results of the x-ray study revealed that in most cases several calcium sulfate and sulfite phases were present, in addition to the expected phases of gypsum and calcium sulfite hemihydrate. In addition, two other major difficulties developed that prevented consideration of quantitative x-ray diffraction techniques: (a) the line broadening that occurred as a consequence of the fine particle size of the sulfur phases and (b) the preferred particle orientation that occurred in sample mounting and resulted, in some cases, in the complete absence of some of the major diffraction peaks from the x-ray patterns, particularly with calcium sulfite hemihydrate. The techniques that have been developed to overcome these difficulties are awkward to use, are time consuming, and create major uncertainties in the final results. It was decided, therefore, that the x-ray study would serve solely as a qualitative indication of the phases present.

The Tennessee Valley Authority (TVA) Shawnee limestone sludges showed strong gypsum peaks (Table A-1). The calcium sulfite hemihydrate, in all cases, was the second most prominent phase in the x-ray patterns, appearing as a moderately strong phase. Residual limestone (calcite) appeared, also, as a weak phase in all samples.

The TVA Shawnee lime sludge displayed an x-ray pattern containing only the calcium sulfite hemihydrate as a strong phase and gypsum as a weak phase. No residual lime or calcium carbonate phases were detected. Specifically, one sample showed an absence of major diffraction peaks for the sulfite phase, whereas other samples showed only an irregular peak intensity distribution for this phase. In nearly every sample, the diffraction peaks were displaced toward greater interatomic spacing.

The Southern California Edison (SCE) Mohave sludge revealed the presence of gypsum as the major phase. In addition, weak patterns of calcium sulfate hemihydrate appeared, indicating a thermal decomposition during drying at 80°C. A moderate calcium carbonate signal was revealed from residual limestone at a measured concentration of 0.5 to 0.3 percent $CaCO_3$ in the slurry (wet basis.)[a]

The General Motors (GM) Parma sludge revealed the calcium sulfate hemihydrate only as a major phase and a weak presence of calcium carbonate. The strong x-ray diffraction peak of the sulfate hemihydrate in this sludge probably indicated the presence of gypsum before oven drying. The line broadening of the x-ray pattern indicated a fine particulate size, and it is probably because of the fine particles that thermal decomposition was complete at drying temperatures. (Thermal decomposition of gypsum to hemihydrate occurs at about 100°C at 1 atm.)

The Arizona Public Service (APS) Company Cholla sludge x-ray pattern consisted primarily of gypsum and calcium sulfite hemihydrate peaks. No residual limestone was detected.

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[a] Private communication, Dr. Alex Weir, Southern California Edison Company, Los Angeles, California.

The Duquesne Light Company (DLC) Phillips lime sludge revealed, in its x-ray pattern, the presence of both calcium sulfate dihydrates and calcium sulfite hemihydrate.

The Utah Power and Light (UPL) Company Gadsby sludge x-ray pattern revealed relatively strong peaks from calcium sulfate hemihydrate and weak peaks of gypsum and calcium carbonate. In addition, the calcium anhydrite phase was revealed. The fine particle size indicated by line broadening in the x-ray pattern probably contributed to its thermal decomposition, as in the GM Parma sludge.

In summary, the x-ray diffraction characterization, while not providing quantitative data, did provide valuable information in identifying phases not otherwise expected in the sludge and also provided semiquantitative data relative to the amount of these phases in the sludge. Line broadening and the absence or irregular distribution of peak intensities inferred the presence of fine particles and the preferred orientation of these particles in the sample, which, relative to ASTM standards, are assumed to be randomly oriented.

A.2 SOLIDS PHASE COMPOSITION BY CHEMICAL ANALYSIS

The composition of the solids fraction of each of the sludges sampled was determined by chemical means and is presented in Table A-2; a description of the analytical techniques used are presented in Appendix C. The wide range in composition for each of the major solid constituents reflects the various design differences that exist among the scrubber systems. Wastes from systems having high-efficiency fly ash collection facilities upstream of the scrubber have compositions that contrast with those from systems having less efficient collection methods. The calcium sulfate content of the waste reflects in each case the capability of the calcium sulfite to oxidize, and this condition usually occurs in the scrubber or reaction tank; exceptions do take place in particular system designs, e.g., the UPL double-alkali system. The amount of total sulfur waste (sulfite and sulfate) does not directly reflect the sulfur content of the coal since other parameters are more influential. For example, the SCE Mohave sludge consists primarily of gypsum, but its coal sulfur content, less than 0.5 percent, is the lowest among the coals sampled. The relative quantity of sulfur waste products in this sludge is primarily a consequence of the low fly ash input to the scrubber. At the other extreme, the TVA Shawnee facilities do not collect fly ash upstream of the scrubber, but the high sulfur content of the coal more than offsets the ratio of fly ash to sulfur waste when compared to other systems with lower sulfur contents. The high sulfur total for each sludge is believed to be a consequence of phase dehydration, which cannot be accurately calculated.

A.2.1 Crystalline Morphology

A portion of sludge solids from each scrubbing facility was selected from the materials prepared for x-ray characterization (Section A.1)

TABLE A-2. PHASE COMPOSITION OF FGD SLUDGES IN WEIGHT PERCENT

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]						[illegible]			
$CaCO_3$	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]					
[illegible]						[illegible]			
NaCl					[illegible]				
[illegible]									[illegible]
Fly Ash	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Total	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

for subsequent examination on the scanning electron microscope (SEM). The dry powders were sprinkled onto an aluminum sample holder and vapor-coated with a thin layer of conducting carbon before insertion into the SEM viewing chamber. A series of photomicrographs were taken of each sludge sample, from which typical examples of the crystalline morphology of the solids content were selected for presentation here. The photomicrographs and description of the solid particulate material characteristic of each sludge are presented in the following text.

A.2.1.1 TVA Shawnee Limestone Sludge

The distribution of particles shown in Figure A-1 represents the solids content of the sludge from the TVA Shawnee turbulent contact absorber (TCA) system using limestone absorbent. This sludge was characterized by large platelets of calcium sulfite hemihydrate and fly ash. A broad range of particle sizes is visible for both phases, with fly ash particles as large as 50-μm diameter and fine particles of less then 0.1-μm diamter. The calcium sulfite phase existed as stacks of platelets with edge dimensions as large as 20 to 50 μm for the largest particles and platelet thickness of approximately 0.1 to 0.5 μm. The occasional observation of a fly ash particle incorporated within a sulfite platelet stack suggests that the agglomeration of sulfite platelets occurred during crystalline formation and was not necessarily a consequence of surface tension agglomeration during drying. In addition to these two phases, large particles of residual limestone and blocky sulfate particles were occasionally seen but were seldom greater than 5 μm in their longest dimension. Other small, unidentifiable particles were seen and could have been magnesium sulfate or calcium chloride phases that crystallized during the drying of the solids. Both of these phases crystallize with a large quantity of chemically bound water. The drying procedure and the vacuum exposure necessary for SEM viewing may cause a disruption of crystalline structure, and the material debris not readily recognizable may be a consequence of this decrepitation.

A.2.1.2 TVA Shawnee Lime Sludge

The photomicrographs shown in Figure A-2 are of sludge particles from the TVA Shawnee venturi spray tower system using lime absorbent. This sludge was characterized by agglomerates of calcium sulfite rosettes and fly ash. The range of fly ash particles was nearly identical to that observed in the TVA Shawnee limestone sludge, but fewer of the large size fractions were observed. The calcium sulfite hemihydrate was found almost exclusively in interwoven clusters, which were unmistakenly a consequence of growth phenomena. Individual platelet size was rarely over 10 μm, with the vast majority being in the range of 5 μm. The platelet thickness was typically 0.1 to 0.5 μm. Fly ash particles were often seen within or associated with a rosette cluster, but this is not interpreted as an indication that fly ash serves as a nucleating site. Generally, particles of calcium sulfite were adhered to fly ash particles; this is not interpreted as a growth phenomena but as a consequence of adherence during drying. In contrast to the limestone system, no calcium carbonate particles were observed, and no clearly discernible gypsum particles were observed. It is presumed that all calcium

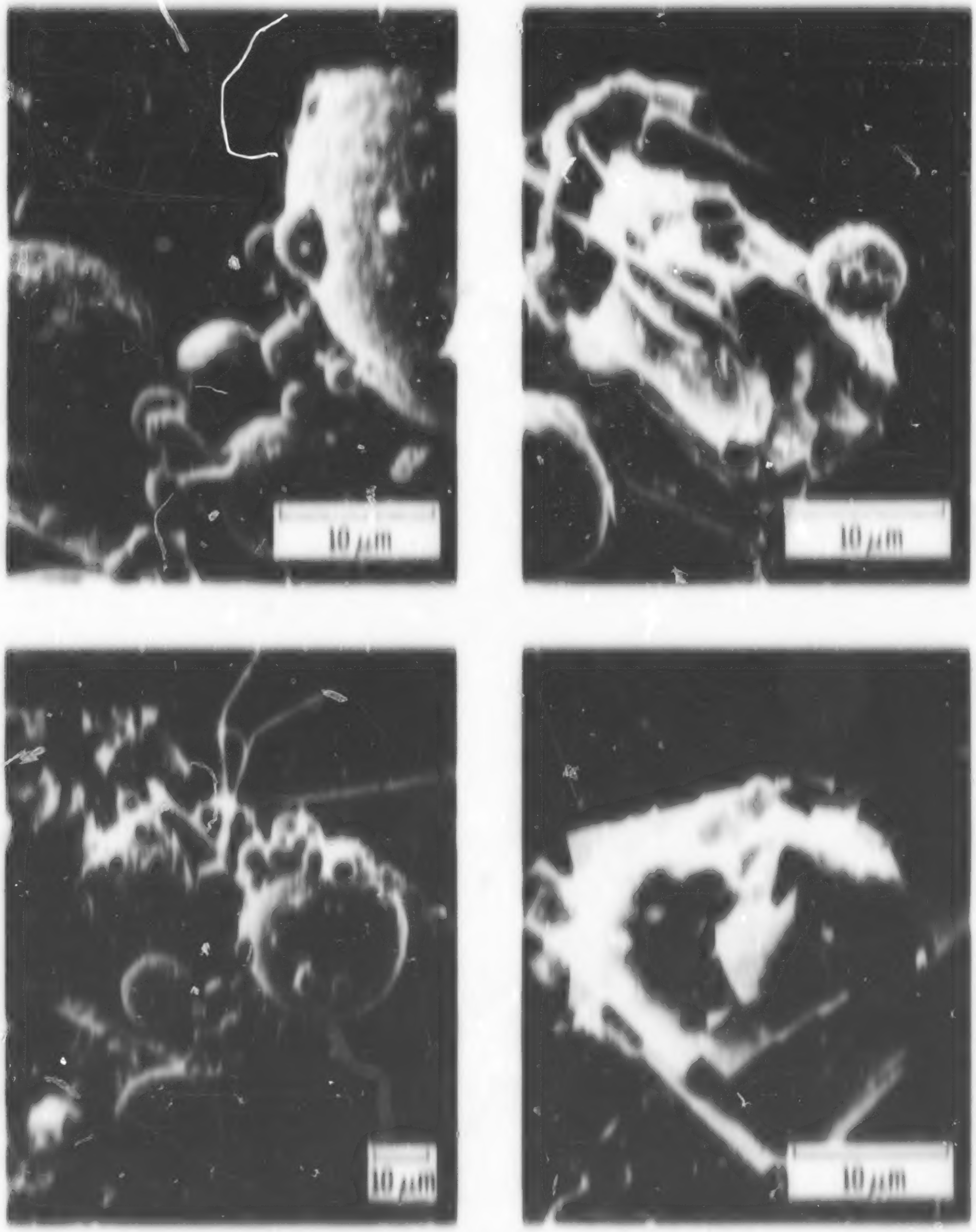

10 μm
10 μm
10 μm
10 μm

Figure A-1. TVA Shawnee limestone sludge.

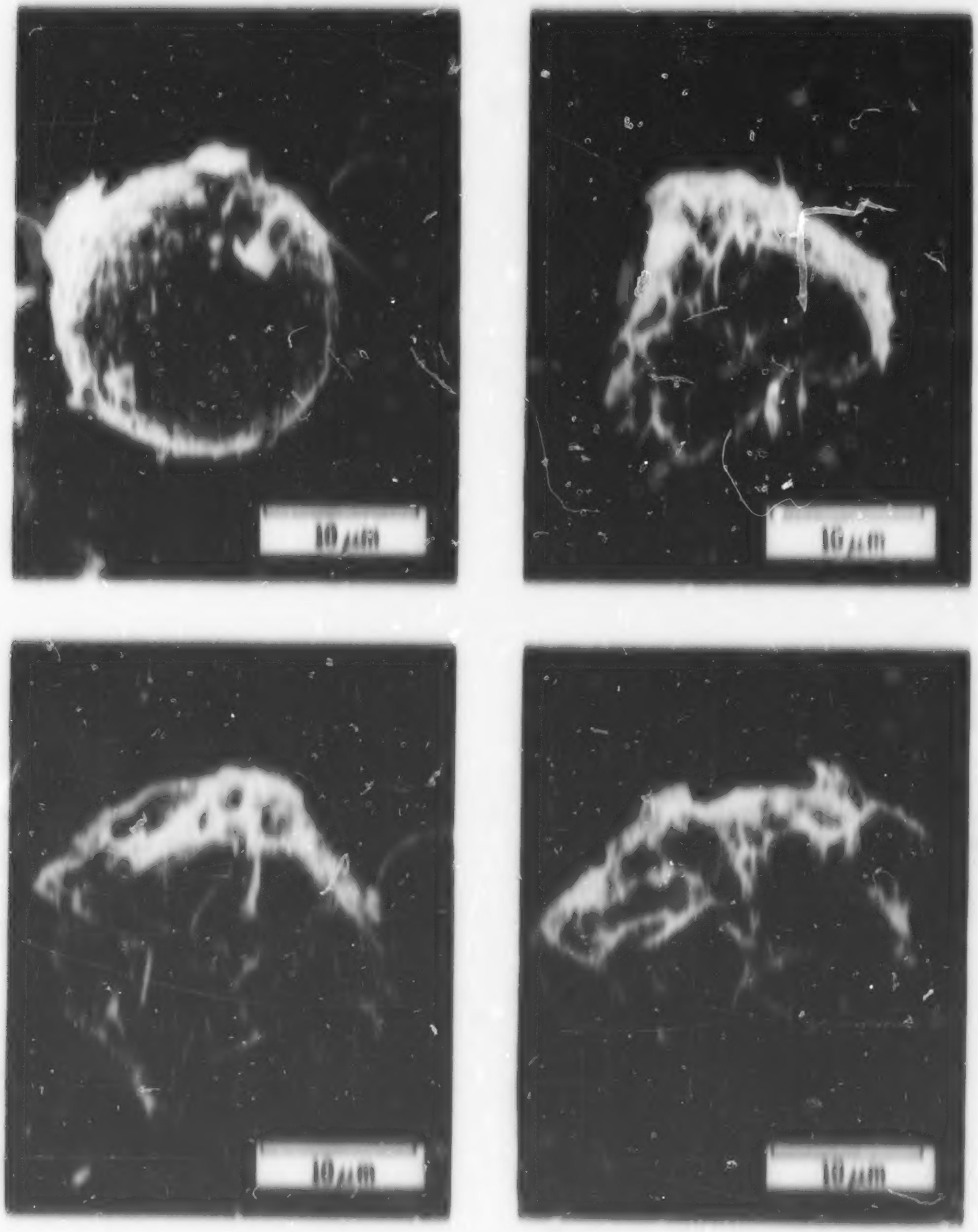

10 μm
10 μm
10 μm
10 μm

Figure A-2. TVA Shawnee lime sludge.

sulfate in the solids fraction existed as a solid solution in the sulfite crystal. The mechanism that caused the differentiation between the calcium sulfite crystal habit in the lime and limestone systems is not understood. Typically, the lime system operated at a higher pH than the limestone system and the scrubber design is different. Whether either of these variables affected the growth habit of calcium sulfite hemihydrate is not fully clear.

A.2.1.3 SCE Mohave Limestone Sludge

The characteristics of the solids content of the SCE Mohave centrifuge cake are shown in Figure A-3. This material was unique among the sludges sampled in several respects. From chemical and x-ray analysis, the major portion of the material was identified as gypsum, but the crystal habit was not typical of gypsum. Instead of lath-like gypsum crystals, the shape of the crystalline phase was bulky and equiaxial. Typically, particle sizes range between 20 and 50 µm, with a few being as large as 100 µm and as small as 5 µm. No calcium sulfite hemihydrate crystals were observed, but some particles appeared to be made up of stacked crystal platelets, possibly sulfite, that had undergone a transformation, probably, by oxidation to sulfate. Other crystals appeared as agglomerates of fine gypsum particles that had grown together into larger particles. A conspicuous absence of fly ash was apparent except for a small quantity of fine particles, typically, less than 1-µm in diameter and found adherent to the surfaces of the gypsum particles. Also, little unreacted limestone was identified although chemical analysis indicated greater than 6 percent calcium carbonate in the sludge solids. (Sampling was done during a limestone depletion run; the residual limestone may have been reduced in particle size during this run such that the limestone present could not be properly identified in the field of view.)

The apparent absence of limestone is understood in relation to the sampling condition, and the small quantity and size range of fly ash are understood relative to the efficiency of the mechanical and electrostatic separators. The multiple-fold recirculation of the system liquors that occurred because of the low sulfur content can explain both the extent of oxidation and the presence of large particles. However, the change in gypsum particle shape, from lath-like to equiaxed particles, is not understood. The morphological changes in crystalline growth reported in the literature are most commonly associated with the chemical poisoning of growth faces. It is presumed that such poisoning of pyramidal growth faces by the high concentration of dissolved salts, primarily sodium chloride, may possibly have promoted relative growth on the prismatic faces.

A.2.1.4 DLC Phillips Lime Sludge

The particles in the photomicrographs presented in Figure A-4 are characteristic of the crystalline phases in the thickner underflow of the DLC Phillips station scrubbing system using lime as the absorbent. The large intergrown crystals of gypsum are ideal as structural plaster. A continual size distribution of gypsum particles was evident, with sizes ranging upward to 100 µm along the length of the gypsum lath and 10 to 20 µm in width. A high concentration of fly ash was present, with the largest particle

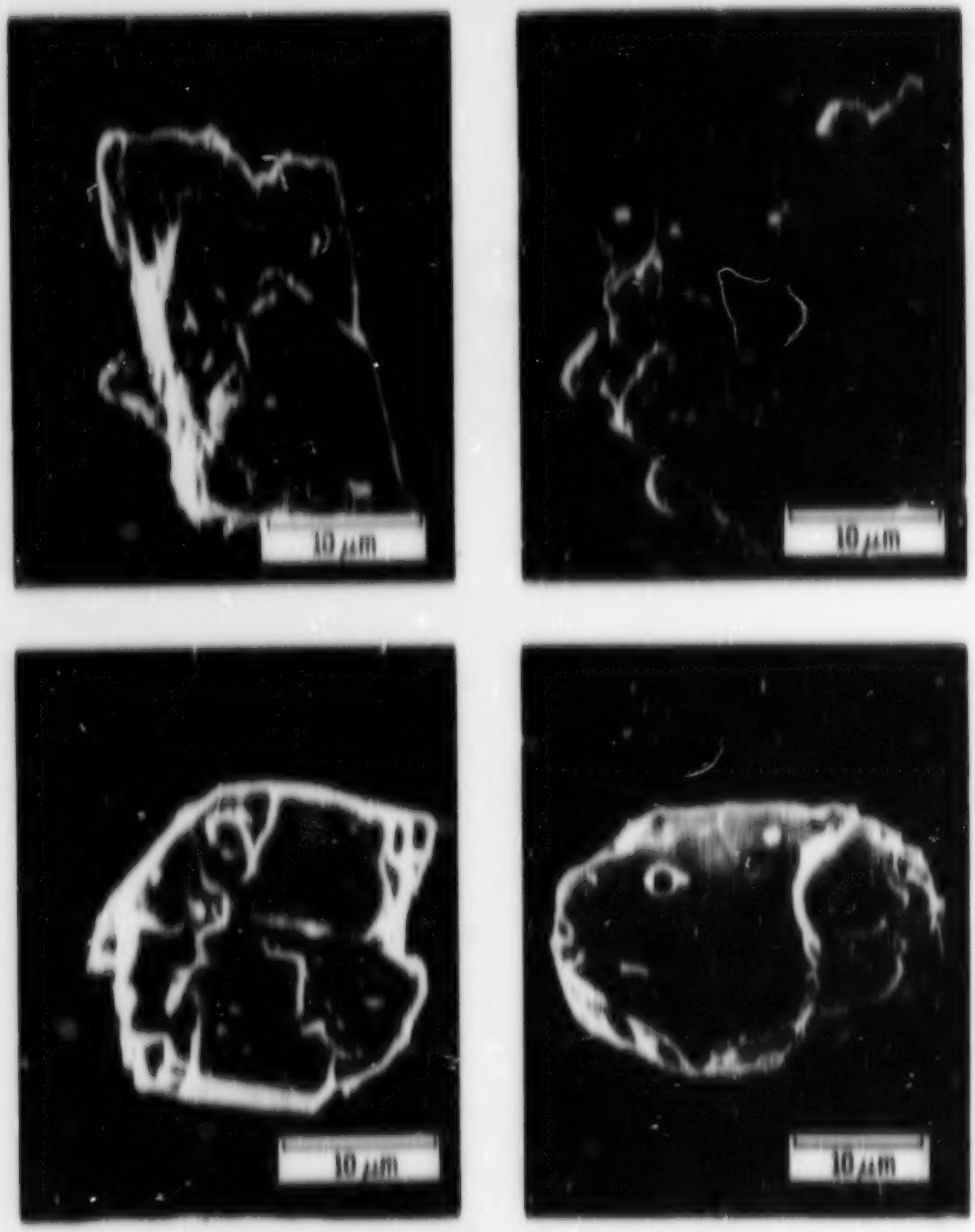

10 μm
10 μm
10 μm
10 μm

Figure A-3. SCE Mohave limestone sludge.

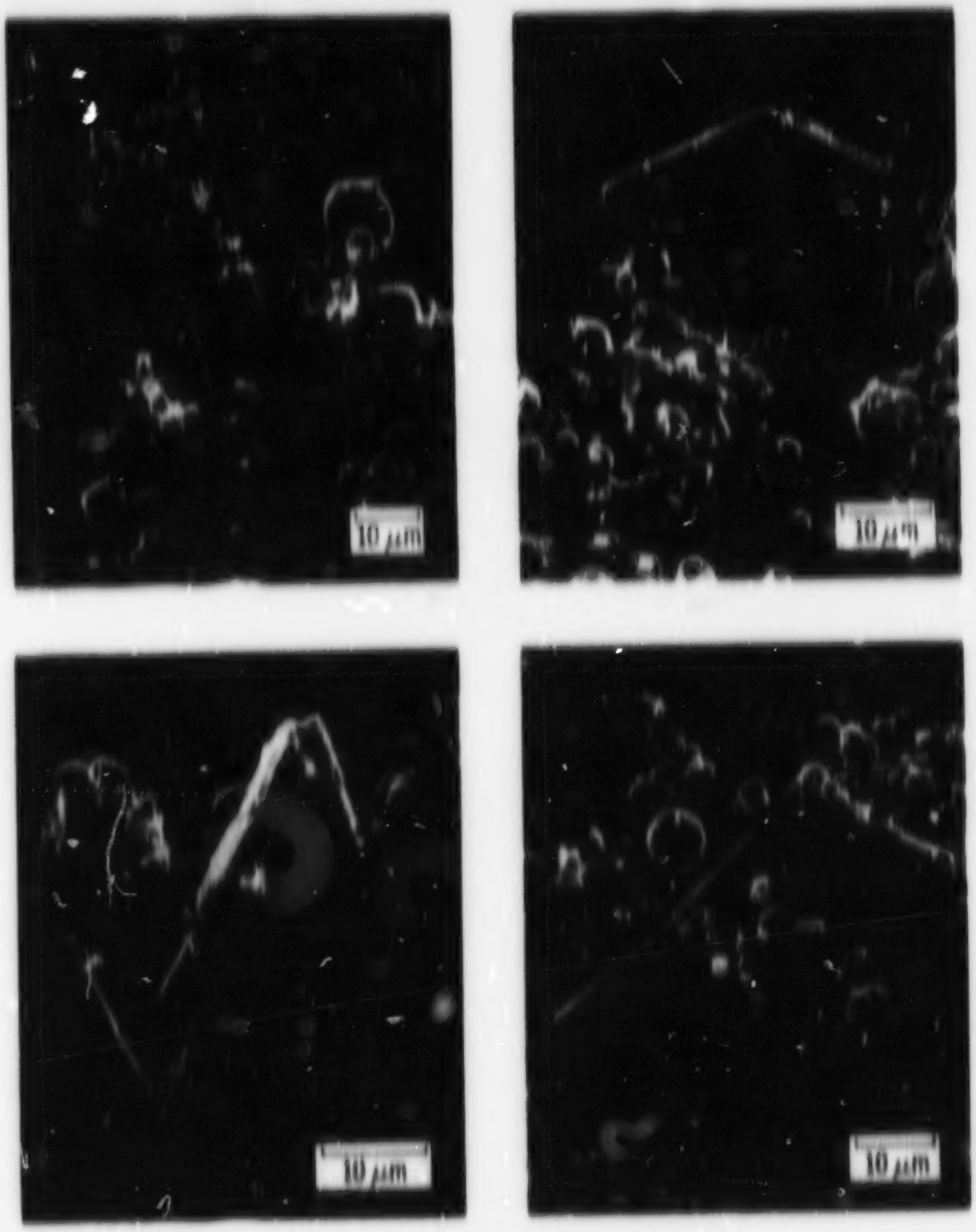

10 μm
10 μm
10 μm
10 μm

Figure A-4. DLC Phillips lime sludge.

diameters ranging upward to 10 to 15 μm and downward to the submicron range. The x-ray and chemical analyses indicated a significant presence of calcium sulfite hemihydrate, but the morphology of this phase, observed in the lime and limestone wastes of the TVA Shawnee system, was not apparent in the DLC Phillips lime waste. There is some solid solubility of the sulfite phase in gypsum, but the solubility limit would not account for the quantity determined by the chemical analysis. An unidentifiable phase, fine in structure, that appeared to be closely associated with fly ash was visible in nearly every field of view and could have been the sulfite phase in a state of decomposition. No other phases were present.

A.2.1.5 APS Cholla Limestone Sludge

The morphology of particles in the APS Cholla waste is represented in Figure A-5. A high portion of the solids content in this waste is fly ash. Particles of fly ash represented a broad range of particle sizes, with diameters of about 15 μm maximum, and downward to less than 0.1 μm. Only one phase of sulfur waste was observed in the APS Cholla waste although several phases were expected from chemical and x-ray diffraction analysis. This phase did not have the lath-like crystal habit of gypsum but rather the thin platelet habit of the calcium sulfite hemihydrate phase. These platelets were dissimilar to the rosette structures of most sulfite crystals and much more like the sulfite crystals of the TVA Shawnee limestone sludge. However, they were not observed in stacks and their thickness was several times greater than those found in the TVA Shawnee limestone sludge. The absence of more recognizable crystalline morphology is not understood even though gypsum was expected as the major phase. A better understanding of the crystal growth phenomena is required in this case.

A.2.1.6 GM Parma Double-Alkali Sludge

The filter cake from the GM system is represented by the photomicrographs in Figure A-6. The most prevalent phase in this material was gypsum that appeared in the form of blocky and lathlike particles, with the largest being about 20 μm along an edge. A distinct decrepitation was apparent in the gypsum particles as a consequence of thermal dehydration during drying. The x-ray analysis revealed the presence of an anhydrous phase which, in this case, was undoubtedly a consequence of decrepitation. A small amount of fly ash was present, with maximum particle size in the range of 5-μm diameter. Calcium sulfite hemihydrate represents about 13 percent of the solid fraction of the filter cake as determined by chemical analysis. This phase appeared in fine agglomerates of individual particles in a rosette-like array. Individual sulfite crystallite sizes were typically from 0.5 to 1.5 μm along an edge, amassed in agglomerates that seldom exceeded 10 μm in equivalent diameters. Some calcium carbonate and sodium sulfate were expected in this material but were not identified.

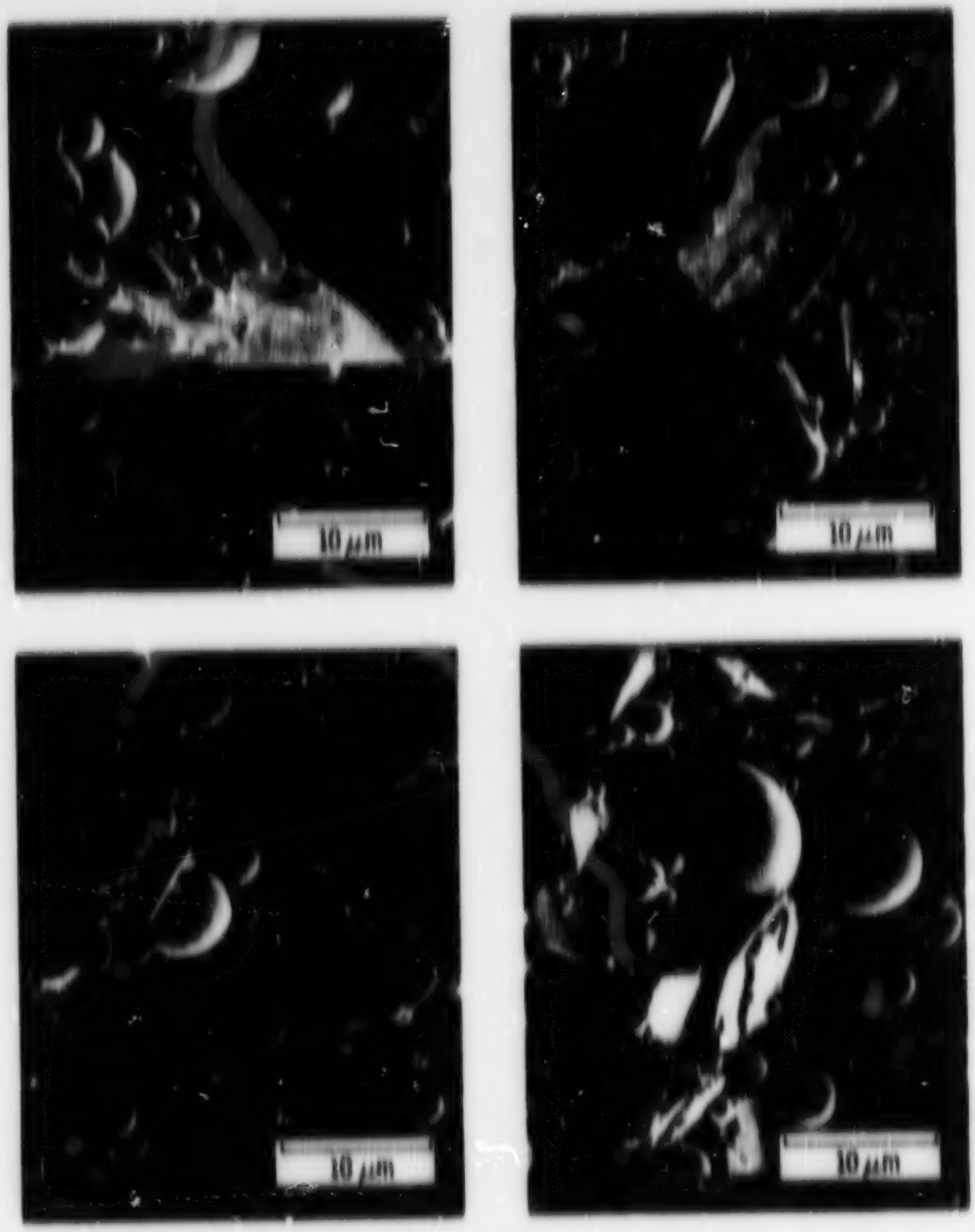

10 μm
10 μm
10 μm
10 μm

Figure A-5. APS Cholla limestone sludge.

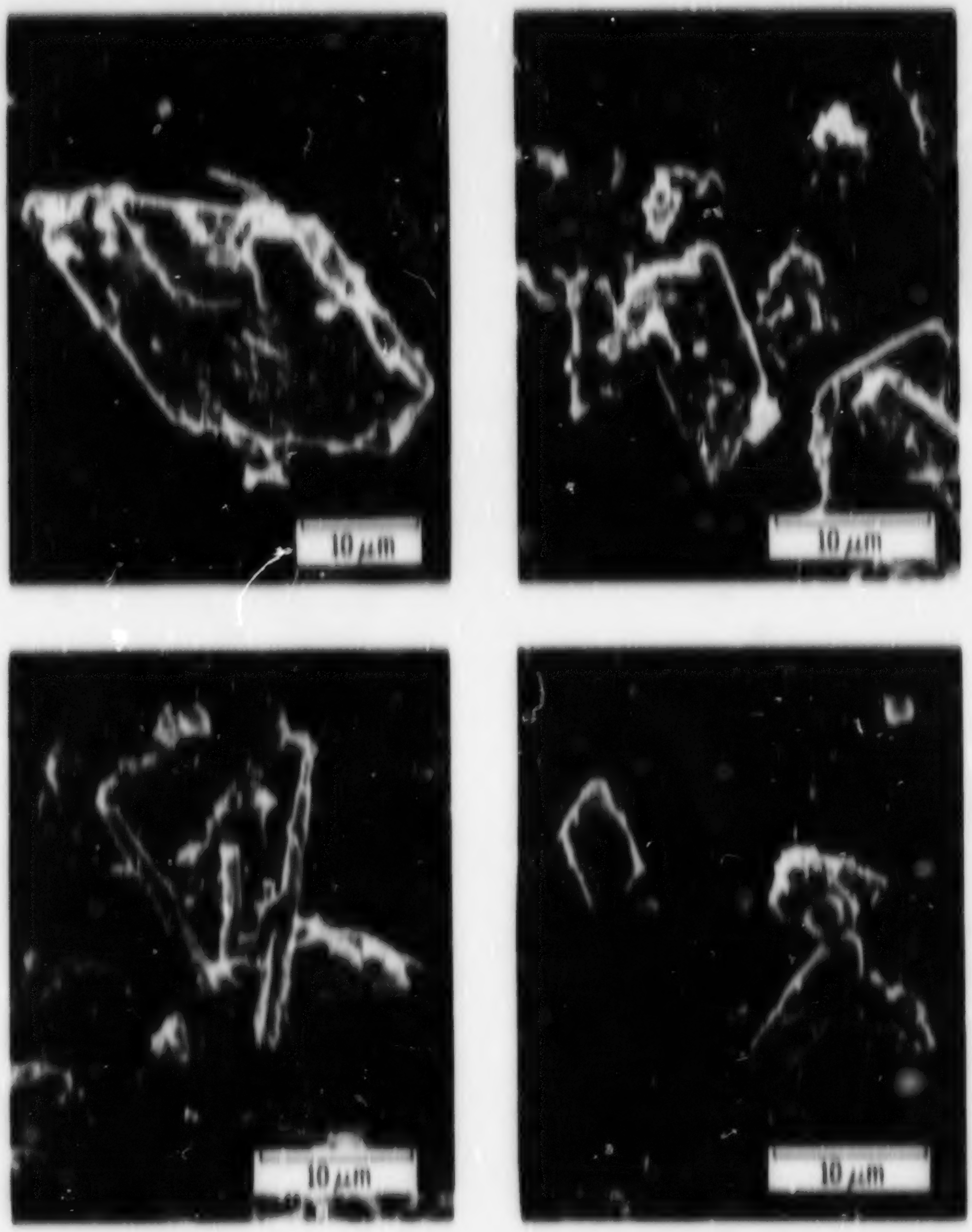

10 µm
10 µm
10 µm
10 µm

Figure A-6. GM Parma double-alkali sludge.

A.2.1.7 UPL Gadsby Double-Alkali Sludge

The filter cake of the UPL Environtech scrubbing system is shown in Figure A-7. This material was similar to the GM double-alkali system in only one feature: the small amount of fly ash in the scrubber solids, with maximum particle size in the range of 5 μm. The phase that represented the major part of the solids was gypsum, which appeared as small crystallites, typically, of 1 to 5 μm in major dimension and agglomerates of more massive particles of nominally 25 μm in diameter. In addition, calcium sulfite hemihydrate particles were observed in greater excess than anticipated from either chemical analyses or x-ray analysis. These particles were morphologically like the calcium sulfite phase observed in the TVA Shawnee lime process as dense clusters of thin platelets. The clustered particles were nominally 25 μm in diameter although the individual platelets were typically 2 to 3 μm along an edge and thin, with a typical thickness of less than 0.2 μm. The x-ray diffraction analysis indicated the presence of a significant quantity of anhydrous calcium sulfate. No separately identified particles of anhydrite were detected, but it is presumed that this phase resulted from the transformation of the smallest size fraction of the gypsum phase. Thus, it was not a phase that could be easily identified, in contrast to the gypsum phase.

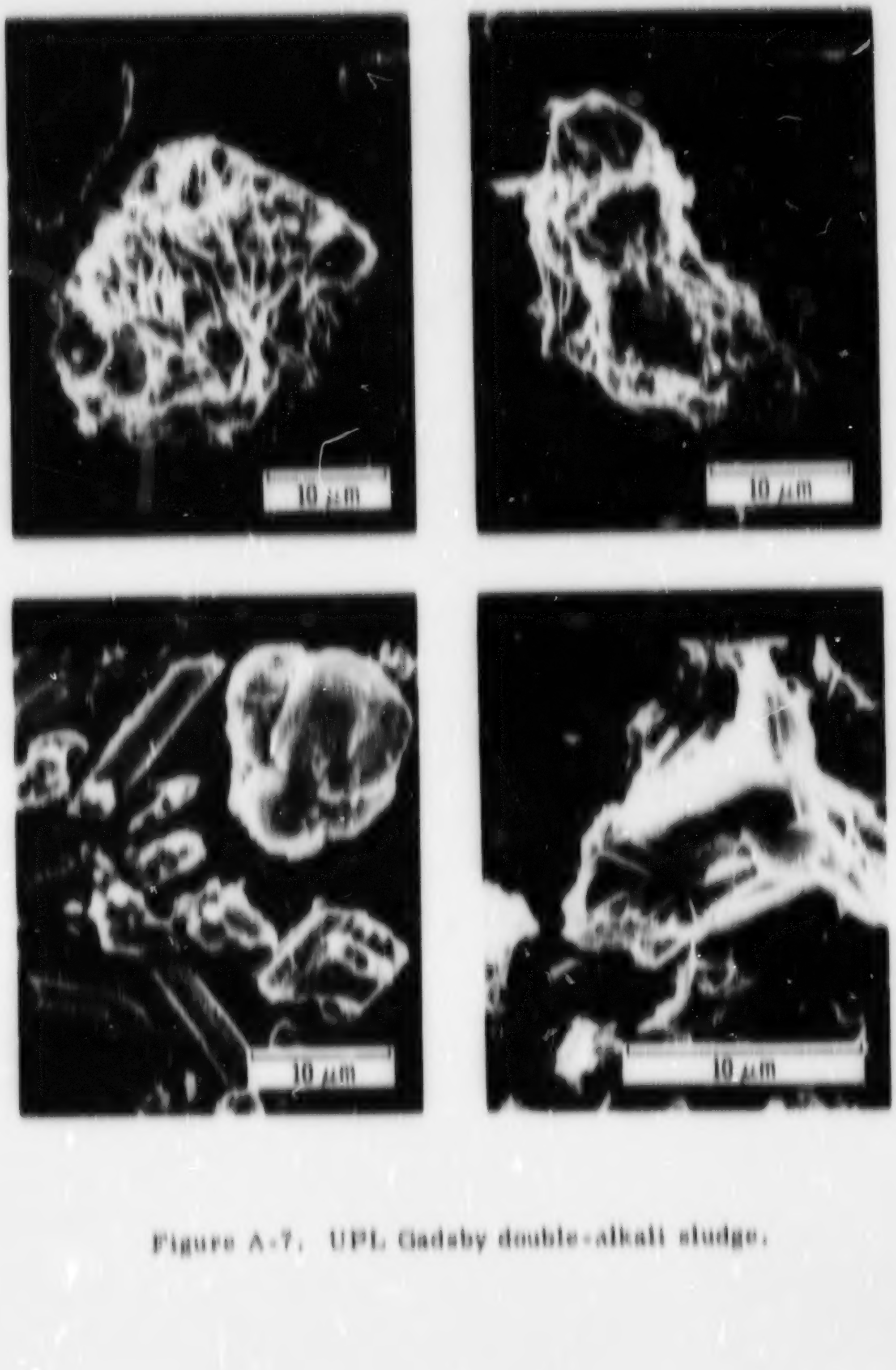

10 μm
10 μm
10 μm
10 μm

Figure A-7. UPL Gadsby double-alkali sludge.

APPENDIX B

DESCRIPTION OF SCRUBBER SYSTEMS

Samples were obtained from the flue gas desulfurization (FGD) scrubbing facilities of seven power plants (Table B-1), representing lime, limestone, and double-alkali systems. This appendix describes these facilities and identifies the sample source locations on the schematic diagrams of the scrubber systems.

TABLE B-1. FGD SYSTEMS SAMPLED AS DATA BASE

Power Plant	Scrubber System	Scrubbing Capacity, MW (equiv)	Coal Source	Absorbent
TVA Shawnee Steam Plant	Venturi and spray tower, prototype	10	Eastern	Lime
TVA Shawnee Steam Plant	Turbulent contact absorber, prototype	10	Eastern	Limestone
Arizona Public Service Company, Cholla Power Plant	Flooded-disk scrubber, wetted film absorber	120	Western	Limestone, fly ash
Duquesne Light Company, Phillips Power Station	Single- and dual-stage venturi	410	Eastern	Lime
General Motors Corporation, Chevrolet-Parma Power Plant	Bubble-cap tower	32	Eastern	Soda ash, lime
Southern California Edison, Mohave Generating Station	Turbulent contact absorber, pilot plant	< 1	Western	Limestone
Utah Power & Light Company, Gadsby Station	Venturi, and mobile bed, pilot plant	< 1	Western	Soda ash, lime

B.1 TVA SHAWNEE POWER STATION

The Tennessee Valley Authority (TVA) Shawnee steam plant provides 150 MW of power from its unit no. 10 coal-fired boiler. Part of the flue gas from unit no. 10 is diverted around the electrostatic precipitators into each of two prototype scrubber systems designed to remove both SO_2 and fly ash. Each scrubbing module can handle 30,000 ACFM of flue gas, equivalent to 10 MW of power generation.

B.1.1 Venturi and Spray Tower

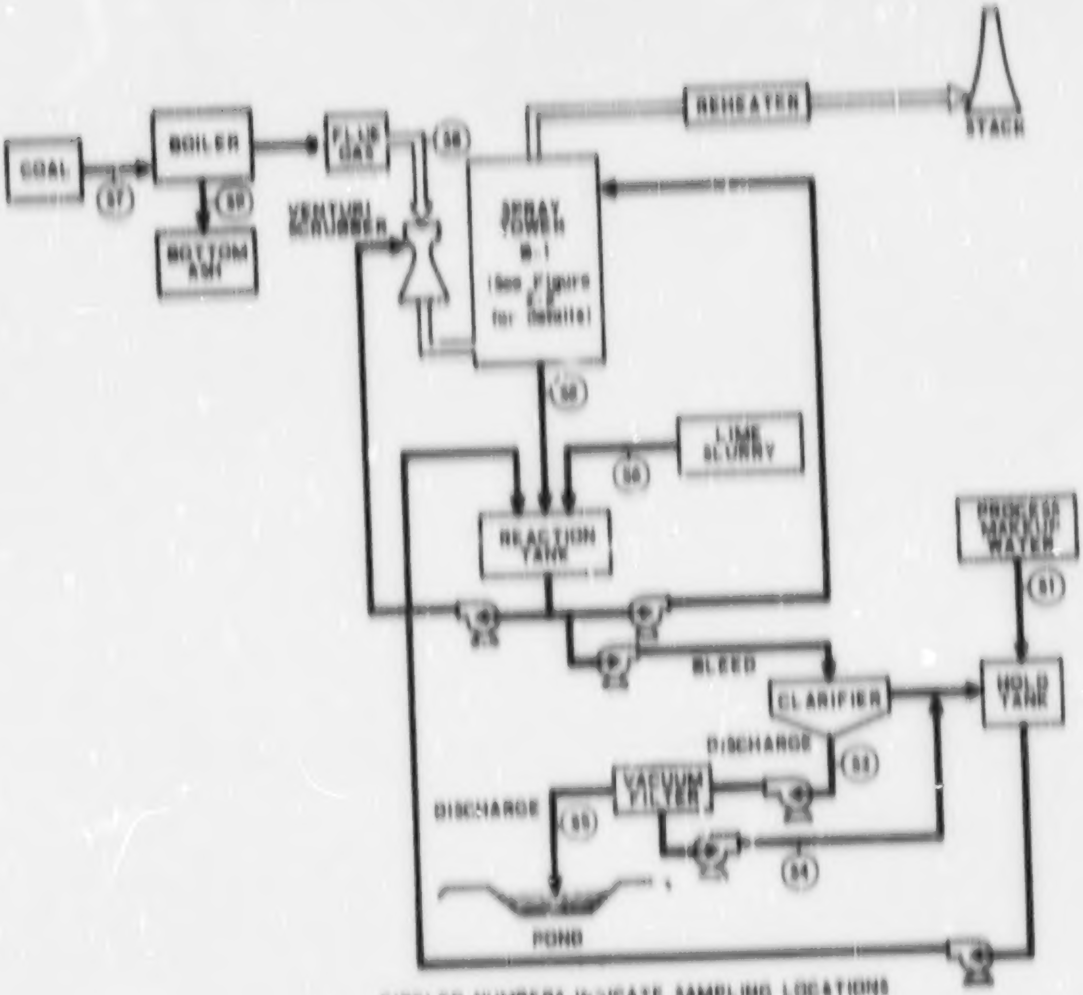
The venturi and spray tower scrubbing system incorporates a dual-stage lime reactant scrubber made by the Chemical Construction Corporation (Chemico) and is shown schematically in Figure B-1. A detailed schematic diagram of the scrubber is shown in Figure B-2.

The first-stage scrubber is a vertical venturi with the flue gas entering at the top. An adjustable plug in the venturi throat controls the scrubber pressure, while a slurry steam, entering above the plug, initiates the removal of particulates. The gas passes into the adjacent after-scrubber spray tower and rises in countercurrent flow against the descending slurry spray injected from four nozzle headers. Slaked lime in the slurry reacts with the SO_2 in the flue gas to form a calcium sulfite precipitate in both the venturi and spray tower. The sulfur waste drains out with the lime-depleted slurry from the lower portion of the spray tower into a reaction tank. The scrubbed flue gas passes through chevron demisters at the top of the tower and through a steam reheater to the stack.

The effluent slurry from the scrubber is collected in a reaction tank, where a holding time delay ranging from 4 to 60 min may be introduced to allow for complete neutralization of the sulfurous acid with the lime slurry feed (pH adjustment) and to permit the growth of calcium sulfite crystals so as to facilitate their removal in the clarifier.

The reaction tank effluent slurry is recirculated to both stages of the scrubber. For the purging of sulfur wastes, a bleedoff from the recirculation line is taken to a 20-ft diameter clarifier. The clarifier overflow goes to a hold tank, where the process makeup water is added; the discharge from this tank is pumped back to the reaction tank, making up for the water lost to the flue gas and that occluded with the solid waste. The underflow from the clarifier is dewatered in a vacuum filter; the clear filtrate is returned to the clarifier overflow circuit; and the filter cake is reslurried and pumped to a disposal pond.

Sample sets were taken on three occasions from the EPA-TVA venturi and spray tower scrubbing system. The operating conditions which these samples represent and the locations at which the samples were taken are presented in Table B-2. The sampling locations are shown on the schematic system diagram, Figure B-1. Samples from location S2, the scrubber effluent, and from location S3, the clarifier effluent, were collected in duplicate. One sample was immediately filtered to separate the liquid from the solid fraction of the slurry; the other sample was collected with the liquid


COAL
57
BOILER
59
BOTTOM ASH
FLUE GAS
58
VENTURI SCRUBBER
SPRAY TOWER B-1 (See Figure 2-2 for Details)
REHEATER
STACK
LIME SLURRY
56
REACTION TANK
PROCESS MAKEUP WATER
61
BLEED
CLARIFIER
HOLD TANK
DISCHARGE
53
VACUUM FILTER
DISCHARGE
55
54
POND

CIRCLED NUMBERS INDICATE SAMPLING LOCATIONS

Figure B-1. Schematic process diagram of the EPA-TVA Shawnee steam plant venturi and spray tower scrubber system showing sampling locations.

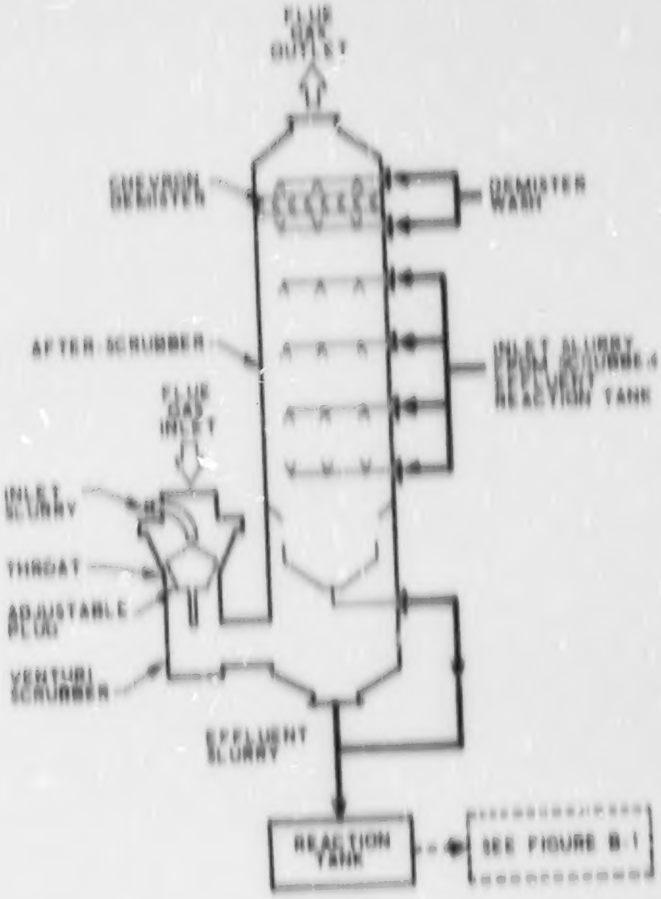

FLUE GAS OUTLET
CHEVRON DEMISTER
DEMISTER WASH
AFTER-SCRUBBER
INLET SLURRY FROM SCRUBBER EFFLUENT REACTION TANK
FLUE GAS INLET
INLET SLURRY
THROAT
ADJUSTABLE PLUG
VENTURI SCRUBBER
EFFLUENT SLURRY
REACTION TANK
SEE FIGURE B-1

Figure B-2. Schematic of EPA-TVA Shawnee steam plant venturi and spray tower scrubber.

TABLE B-3. TVA SHAWNEE VENTURI AND SPRAY TOWER SCRUBBER SYSTEM LIME PROCESS OPERATING CONDITIONS AND SAMPLE LOCATIONS

Operating Condition	19 Mar 1974	16 May 1974	27 Jun 1974
Coal, % sulfur	3.4	3.4	3.4
Gas Flow Rate,			
$m^3 sec^{-1}$	11.8	11.8	11.8
ACFM	25,000	25,000	25,000
Equivalent Power, MW	8.3	8.3	8.3
SO_2 Input, ppm	36,000	3,400	2,700
SO_2 Removal, %	93	78	84
pH Control	8.0	8.0	8.0
Dust Input,			
$g (m)^{-3}$	8.0	8.0	8.0
$gr (scf)^{-1}$	3.5	3.5	3.5
Scrubber Effluent, solids %	8	8	8
Clarifier Underflow, solids %	18	18	18
Filter Cake, solids %	45	45	45
Liquid-to-Gas Ratio,			
$gpm (1000 cfm)^{-1}$	54	54	54

Sampling Location[a]	19 Mar 1974	16 May 1974	27 Jun 1974
Process Makeup Water	S1		
Scrubber Effluent	S2	S2	S2
Clarifier Effluent	S3	S3	S3
Vacuum Filter Filtrate	S4	S4	S4
Vacuum Filter Cake	S5		
Lime Slurry	S6		
Coal	S7		
Fly Ash	S8		
Bottom Ash	S9		

[a] All samples were taken by TVA personnel.

retained with the solid. In every case, both samples were chemically characterized.

B.1.2 Turbulent Contact Absorber (TCA)

The TCA limestone scrubbing process is operated in parallel with the venturi lime process unit described in the previous section and is shown schematically in Figure B-3. This system is also supplied with 30,000 (maximum) ACFM of flue gas from boiler unit no. 10, diverted around the electrostatic precipitators, and is designed to scrub both SO_2 and flue dust. The TCA scrubber, manufactured by Universal Oil Products (UOP) uses a fluidized bed of low density spheres to provide liquid gas contact surfaces and is shown in detail in Figure B-4.

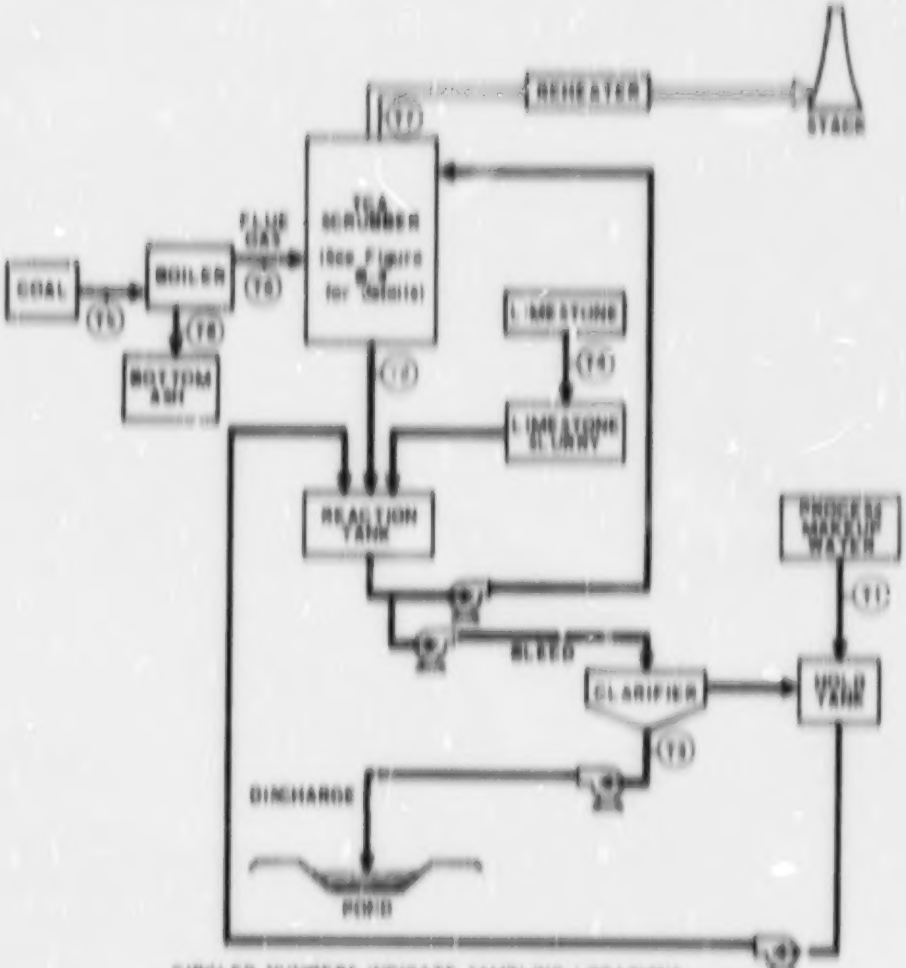
The flue gas enters laterally near the bottom of the scrubber tower and rises in a countercurrent flow against the descending scrubbing slurry. Intimate contact between the two phases is obtained in a three-deck central section, partially packed with mobile plastic spheres levitated by the gas flow between lower and upper retaining grids. Crushed limestone in the slurry reacts with SO_2 in the flue gas to produce a precipitate of calcium sulfite and releases CO_2 to the flue gas. In a secondary reaction, the excess O_2 in the flue gas combines with sulfite ion to produce sulfate ion, which forms a precipitate with calcium ion.

In the upper portion of the tower, two sets of nozzles are installed: One is directed downward and sprays the slurry over the rising gas; the other, a stream sparge, is directed upward against the underside of a Koch tray and keeps it from clogging. The Koch tray breaks up the flow of gas as it impinges on a demister placed in the uppermost part of the scrubber. The wet flue gas passes out at the top of the scrubber and through a steam reheater into the stack.

The slurry, after reacting with the SO_2, drains from the bottom of the scrubber into a reaction tank, where it may be held to provide a recirculation residence time of 5 to 20 min, allowing the sulfite precipitation to proceed further toward completion. From the reaction tank, the recirculation loop carries the slurry back to the scrubber spray nozzles. In addition, fresh limestone slurry is added to the reaction tank to replace that depleted by the SO_2 reaction.

A bleedoff from the reaction tank discharge removes part of the slurry to the clarifier tank where a separation of liquids and solids takes place. The clear overflow is returned to the reaction tank via a hold tank where process makeup water is added to replenish stack and pond loss. The underflow from the clarifier is pumped as a sludge to a disposal pond.

Sample sets were taken on four occasions from the TCA scrubbing system. Table B-3 presents the operating conditions for each sampling occasion and the sample locations shown on the schematic process diagram in Figure B-3. The scrubber effluent sample T2 and the clarifier effluent sample T3 were obtained in duplicate. One sample was filtered immediately at the time of sampling; the other sample was collected with the liquid retained with the solid. Both samples, in every case, were chemically characterized.


REHEATER
STACK
T7
TCA SCRUBBER (See Figure B-2 for details)
FLUE GAS
COAL
T5
BOILER
T6
T8
BOTTOM ASH
T2
LIMESTONE
T4
LIMESTONE SLURRY
REACTION TANK
PROCESS MAKEUP WATER
T1
BLEED
CLARIFIER
HOLD TANK
T3
DISCHARGE
POND

CIRCLED NUMBERS INDICATE SAMPLING LOCATIONS

Figure B-1. Schematic process diagram of the EPA-TVA Shawnee steam plant TCA system showing sampling locations.

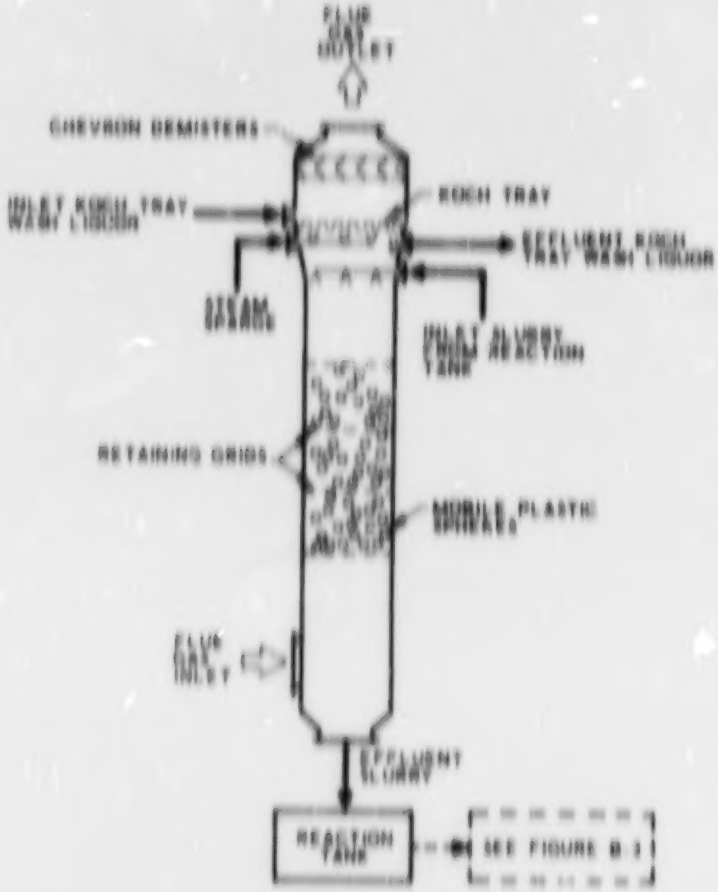

FLUE GAS OUTLET
CHEVRON DEMISTERS
INLET KOCH TRAY WASH LIQUOR
KOCH TRAY
EFFLUENT KOCH TRAY WASH LIQUOR
STEAM SPARGE
INLET SLURRY FROM REACTION TANK
RETAINING GRIDS
MOBILE PLASTIC SPHERES
FLUE GAS INLET
EFFLUENT SLURRY
REACTION TANK
SEE FIGURE B-3

Figure B-4. Schematic of EPA-TVA Shawnee steam plant TCA scrubber.

TABLE B-3. TVA SHAWNEE TCA SCRUBBER SYSTEM LIMESTONE PROCESS OPERATING CONDITIONS AND SAMPLE LOCATIONS

Operating Condition	1 Feb 1973	12 Jul 1973	27 Nov 1973	15 Jun 1974
Coal, % sulfur			3.4	3.4
Gas Flow Rate,				
$m^3 sec^{-1}$	9.7	9.7	9.7	9.7
ACFM	20,300	20,000	20,500	20,500
Equivalent Power, MW	6.8	6.7	6.9	6.8
SO_2 Input, ppm	2,400	2,400	2,700	2,400
SO_2 Removal, %	83	74	83	86
pH Control	5.9	5.7	5.9	5.5
Dust Input,				
$g (m)^{-3}$	5	8	8	8
$gr (scf)^{-1}$		3.5	3.5	3.5
Scrubber Effluent solids %	7.0	3.5	16.0	8.0
Liquid-to-Gas Ratio,				
$gpm (1000 cfm)^{-1}$	43.6	40.0	54.6	54.6

Sampling Location[a]	1 Feb 1973	12 Jul 1973	27 Nov 1973	15 Jun 1974
Process Makeup Water	T1	T1	T1	T1
Scrubber Effluent	T2	T2	T2	T2
Clarifier Effluent	T3	T3	T3	T3
Limestone	T4	T4	T4	
Coal	T5	T5	T5	T5
Fly Ash to Scrubber	T6	T6	T6	
Fly Ash from Scrubber	T7			
Bottom Ash	T8	T8	T8	

[a] All samples were taken by TVA personnel.

B.2 SOUTHERN CALIFORNIA EDISON (SCE) COMPANY MOHAVE STATION TCA SCRUBBER SYSTEM

The SCE Mohave station limestone scrubbing system at the time of sampling was operating on a pilot-plant scale prior to the construction of a full-scale FGD scrubbing installation. The investigation described here was limited to the pilot operation of a TCA scrubber manufactured by UOP, and it is not known whether it is applicable to the full-scale TCA unit subsequently installed at Mohave. The pilot plant scrubbing system is shown schematically in Figure B-5.

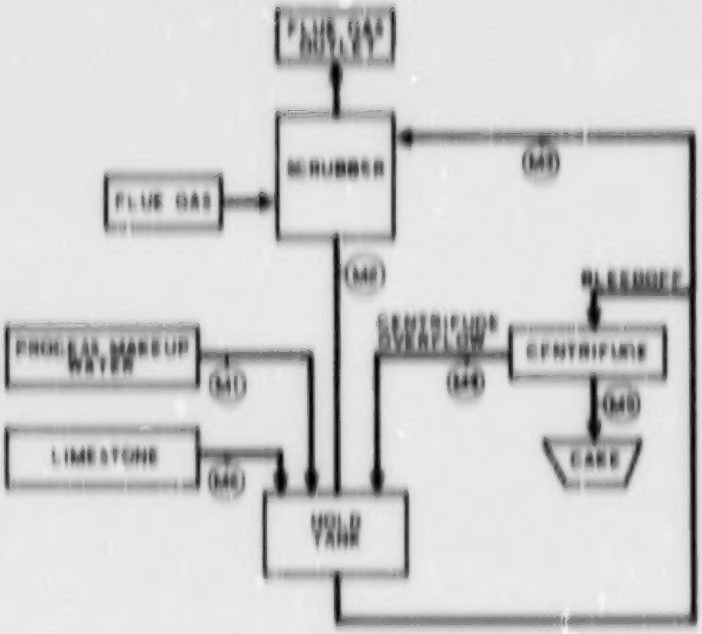
The scrubber is a three-stage TCA tower, 27 ft high, 19 in. in diameter, and rated at approximately 0.5-MW equivalent power generation. The primary reaction between the recirculating limestone slurry and SO_2 in the flue gas yields a relatively insoluble calcium sulfite precipitate, which undergoes subsequent oxidation to the sulfate phase. Slurry from the scrubber is retained in the recirculation loop between the scrubber and hold tank for an appreciable time because the low-sulfur coal burned and the low particulate concentration in the flue gas do not produce a large quantity of solids relative to the quantity of flue gas scrubbed. Thus, only a small bleed stream from the recirculation loop is necessary to maintain a constant solids level in the recirculating slurry.

This bleed is pumped to a centrifuge that separates liquid from a solid cake. The liquor is returned to the hold tank, at which point process makeup water is added to compensate for water lost to the stack and centrifuge cake. The hold tank serves not only as a surge tank but as a reaction tank to which fresh limestone reactant is added. The centrifuge cake is discharged to a disposal site.

A single set of samples was taken at the SCE Mohave station for analysis. Operating conditions at the time of sampling were defined as limestone depletion tests, and no attempt was made to maintain a controlled slurry concentration level. The sample locations are identified in Table B-4 and are shown on the schematic system diagram in Figure B-5. All samples were taken by Bechtel personnel.

TABLE B-4. SCE MOHAVE TCA SCRUBBER SYSTEM SAMPLE LOCATIONS

Sampling Location	30 Mar 1973
Process Makeup Water	M1
Scrubber Effluent	M2
Scrubber Recirculation	M3
Centrifuge Centrate	M4
Centrifuge Cake	M5
Limestone	M6


FLUE GAS OUTLET
SCRUBBER
M3
FLUE GAS
M2
BLEEDOFF
CENTRIFUGE OVERFLOW
CENTRIFUGE
PROCESS MAKEUP WATER
M1
M4
M5
LIMESTONE
M6
CAKE
HOLD TANK

CIRCLED NUMBERS INDICATE SAMPLING LOCATIONS

Figure B-5. Schematic process diagram of the SCE Mohave station TCA pilot plant scrubber system showing sampling locations.

B.3 DUQUESNE LIGHT COMPANY (DLC) PHILLIPS STATION SINGLE- AND DUAL-STAGE VENTURI SCRUBBER SYSTEM

The DLC Phillips power station scrubber system was designed to scrub the total flue gas produced by the full plant capacity of 187-MW generating power with three of four parallel venturi scrubber modules such that one module is available as reserve. Three modules are single-stage venturi scrubbers designed primarily for particulate removal; the fourth module consists of a dual-stage venturi scrubber designed to remove fly ash in the first stage and SO_2 in the second stage. A schematic of the process diagram of the single-stage system is presented in Figure B-6, and the dual-stage system is presented in Figure B-7. Details of the venturi scrubber manufactured by Chemico and used in both systems are shown in Figure B-8.

The flue gas from the boilers pass through mechanical and electrostatic dust collectors which remove the bulk of the fly ash but allow 10 to 30 percent of the fly ash to enter the first-stage scrubber (or single scrubber). Flue gas enters the venturi scrubber at the top, passes through a venturi throat, and emerges laterally at the bottom. Half of the recirculating scrubber liquor is introduced above the cone, forming the center of the throat; the other half is sprayed in through tangential nozzles. In the dual-stage system, the flue gas is pumped to a second venturi operating in an identical manner and then emerges through a reheater to the exhaust stack. In the single-stage system, the flue gas is passed through mist eliminators and the reheater before entering the exhaust stack.

In the first-stage scrubber (or single scrubber), intimate contact between liquor and flue gas occurs in the throat area, where fly ash and about 60 percent of the SO_2 are removed. The second-stage scrubber removes an additional 30 percent of the SO_2 in the flue gas. The lower part of the scrubber separates liquor from the flue gas and serves as a reaction vessel where sulfurous acid commences to react with lime to precipitate a calcium sulfite waste. Half of the slaked lime slurry used as the absorbent is introduced into the system at this point; the other half is introduced into the clarifier, which receives the bleed from the recirculating scrubber slurry from all scrubber modules. Overflow from the clarifier is pumped into the recirculation system; the underflow from the clarifier is pumped to an interim disposal pond. A supernate from the pond is returned to the clarifier. Process make-up water enters the system in the lime slurry, pump seal water, and fan and demister sprays.

Sample sets were taken on two occasions from the DLC Phillips station scrubber system. The first sample set was taken at a time when only the single-stage system was operating; the second sample set was taken at a time when the dual-stage system was in operation. The operating conditions for both sampling occasions and the description of the sample locations are presented in Table B-5. The sample locations are also shown in Figures B-6 and B-7. All samples were taken by DLC personnel.

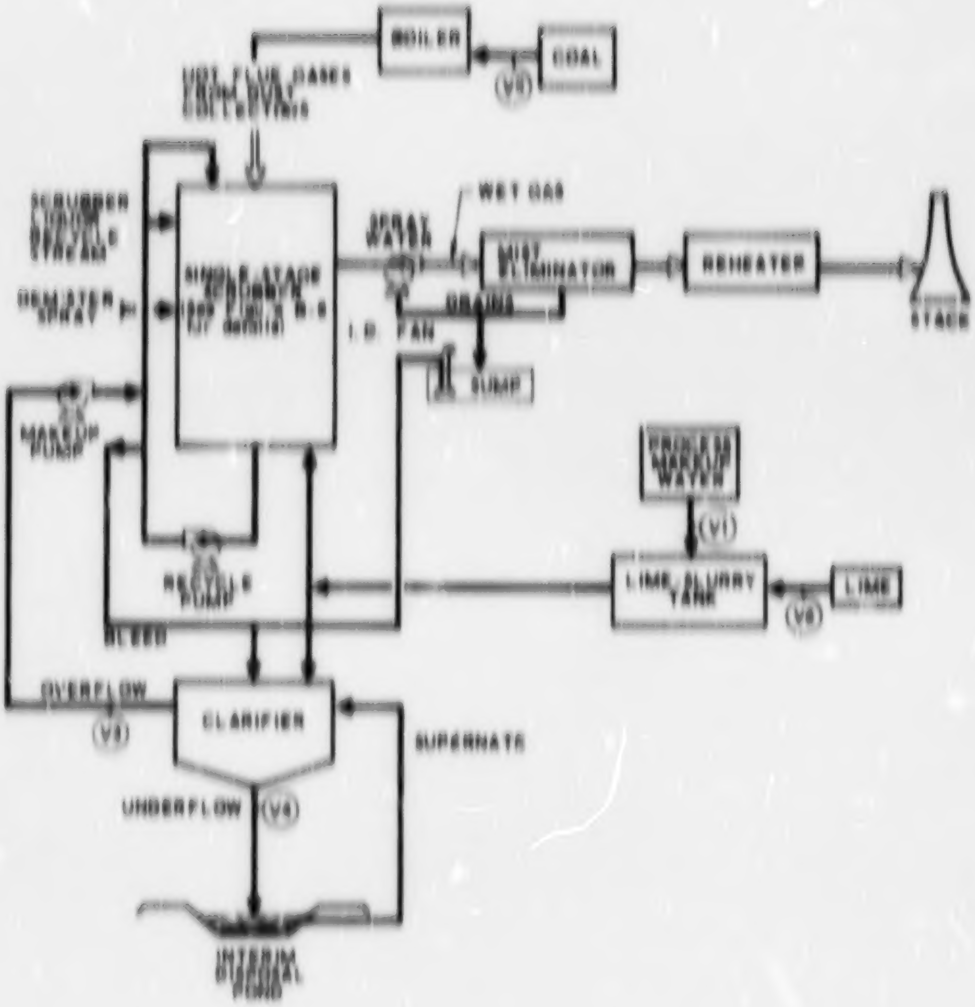

BOILER
COAL
(V5)
HOT FLUE GASES FROM DUST COLLECTORS
SCRUBBER LIQUOR RECYCLE STREAM
DEMISTER SPRAY
SINGLE-STAGE SCRUBBER
WET GAS
SPRAY WATER
MIST ELIMINATOR
REHEATER
STACK
DRAINS
I.D. FAN
SUMP
MAKEUP PUMP
PROCESS MAKEUP WATER
(V1)
RECYCLE PUMP
LIME SLURRY TANK
LIME
(V6)
BLEED
OVERFLOW
(V3)
CLARIFIER
SUPERNATE
UNDERFLOW
(V4)
INTERIM DISPOSAL POND

Figure B-6. Schematic process diagram of the DLC Phillips station single-stage scrubber system showing sampling locations.

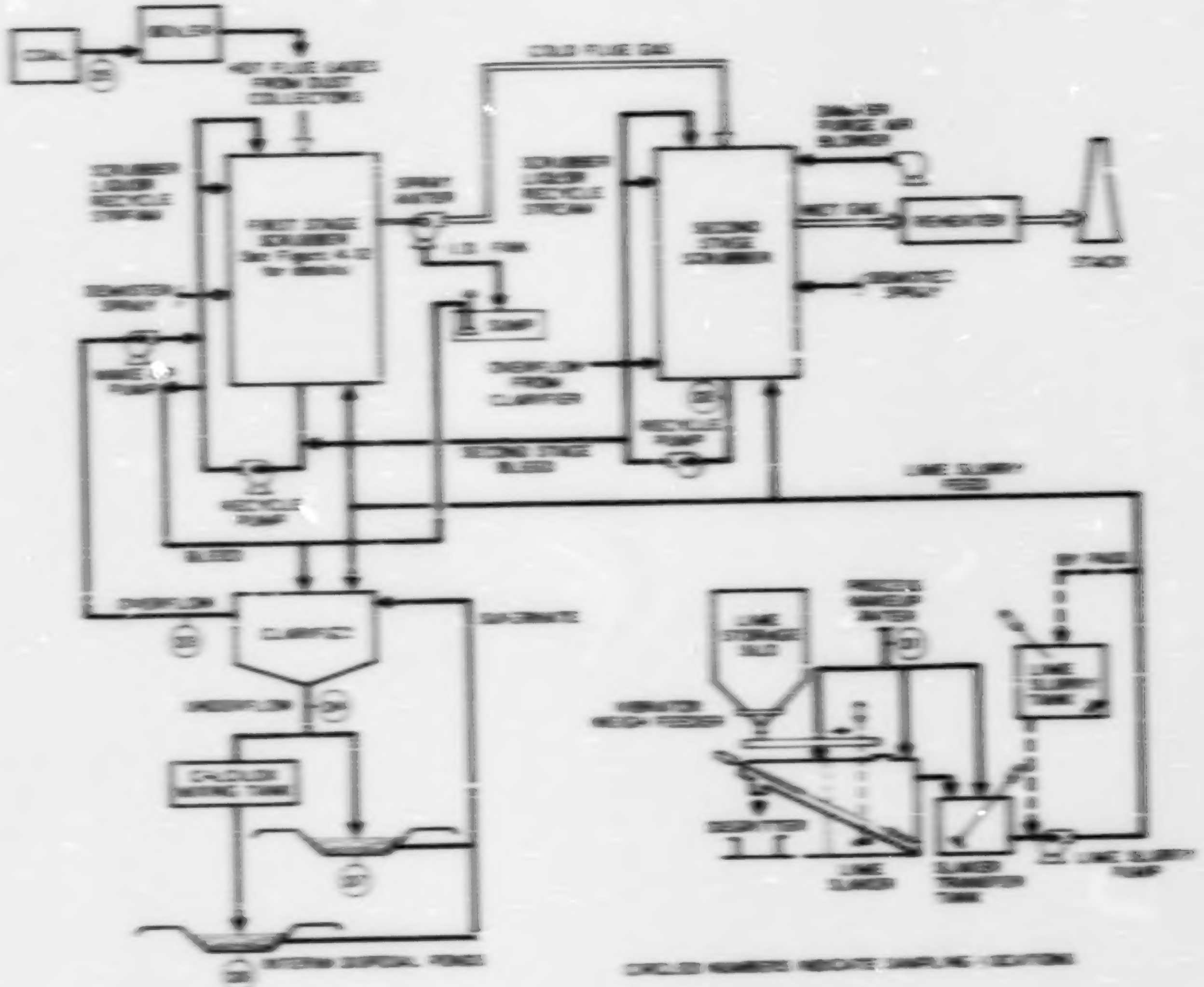

COAL
BOILER
HOT FLUE GASES FROM DUST COLLECTORS
COLD FLUE GAS
SCRUBBER LIQUOR RECYCLE STREAM
FIRST STAGE SCRUBBER
SPRAY WATER
I.D. FAN
SUMP
RECYCLE PUMP
BLEED
SECOND STAGE BLEED
OVERFLOW FROM CLARIFIER
SECOND STAGE SCRUBBER
WET GAS
REHEATER
STACK
LIME SLURRY FEED
OVERFLOW
CLARIFIER
UNDERFLOW
SUPERNATE
INTERIM DISPOSAL POND
LIME STORAGE SILO
LIME SLAKER
LIME SLURRY TANK
LIME SLURRY PUMP
BY PASS
CIRCLED NUMBERS INDICATE SAMPLING LOCATIONS

Figure B-7. Schematic process diagram of the DLC Phillips station dual-stage scrubber system showing sampling locations.

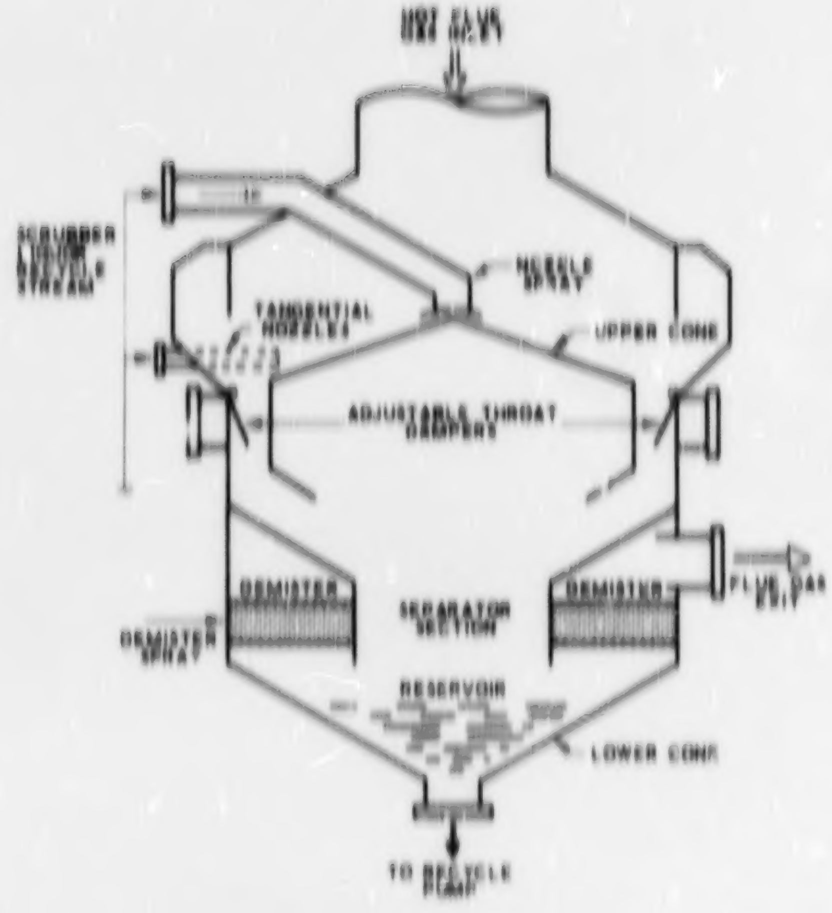

HOT FLUE GAS INLET
SCRUBBER LIQUOR RECYCLE STREAM
NOZZLE SPRAY
TANGENTIAL NOZZLES
UPPER CONE
ADJUSTABLE THROAT DAMPERS
DEMISTER
SEPARATOR SECTION
DEMISTER
FLUE GAS EXIT
DEMISTER SPRAY
RESERVOIR
LOWER CONE
TO RECYCLE PUMP

Figure B-8. Schematic of DLC Phillips power station venturi scrubber.

TABLE B-5. DLC PHILLIPS SCRUBBER SYSTEM OPERATING CONDITIONS AND SAMPLE LOCATIONS

Operating Condition	4 Oct 1973	17 Jun 1974
Coal, % sulfur	2.0	2.0
Gas Flow Rate,		
m^3 sec^{-1}	274	236
ACFM	580,000	500,000
Equivalent Power, MW	145	120
SO_2 Input, ppm	1,400	1,400
SO_2 Removal, %	60	70
pH Control	6.0	6.0
Dust Input,		
g $(m)^{-3}$	0.57	0.57
gr $(scf)^{-1}$	0.25	0.25
Scrubber Effluent, solids %	5	5
Liquid-to-Gas Ratio,		
gpm $(1000\ cfm)^{-1}$	29.9	29.9

Sampling Location	4 Oct 1973	17 Jun 1974
Process Makeup Water	V1	D1
Scrubber Effluent		D2
Clarifier Overflow	V3	D3
Clarifier Effluent	V4	D4
Coal	V5	D5
Lime	V6	
Interior Pond Sludge		D7
Interior Pond Sludge, with Calcilox		D8

B.4 ARIZONA PUBLIC SERVICE (APS) COMPANY CHOLLA STATION FLOODED DISK SCRUBBER (FDS) AND PACKED ABSORPTION TOWER SCRUBBER SYSTEM

The APS Cholla scrubber system utilizes limestone scrubbing to remove SO_2 and particulates from flue gas produced by a 120-MW boiler. Two scrubbers are installed in parallel, each handling 60-MW equivalent power and sharing a common limestone feed and scrubbing liquor circulation. One scrubber is filled with a wet film packing for high SO_2 absorption efficiency; the other is unpacked and operates as a spray tower. The packed scrubber unit is illustrated in Figure B-9; details of this scrubber are shown in Figure B-10.

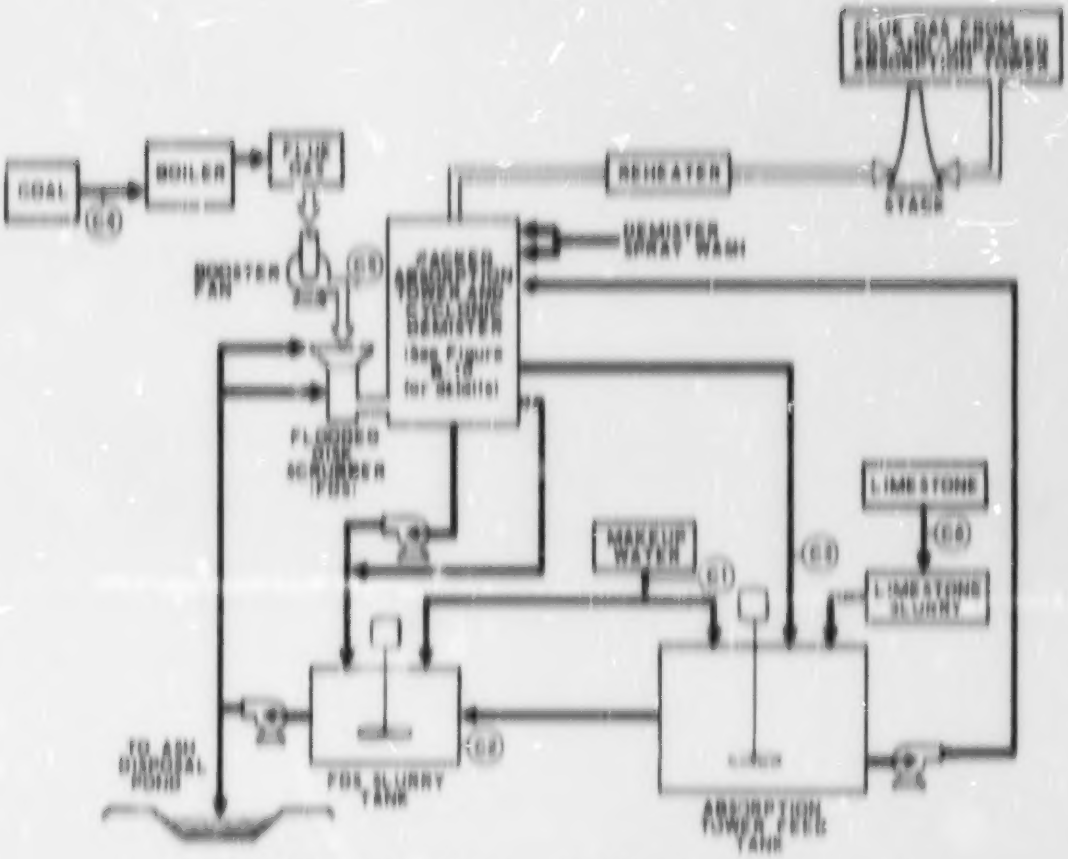
Prior to entering the scrubbers, the flue gas has about 80 percent of its dust removed by a mechanical collector system. A forced-draft booster fan then forces the flue gas into the first scrubbing stage, a venturi-type FDS designed to remove the remaining fly ash by injecting the FDS slurry tangentially above the venturi throat and at the variable setting disk. The FDS slurry passes into the absorber tower, where it is separated from the gas in a cyclonic demister section, and drains out the bottom to the FDS slurry tank.

The flue gas, containing 70 to 85 percent of the initial SO_2, moves upward through the absorption section of the tower, where it comes in contact with a wet-film packing and is scrubbed by the counterflowing limestone slurry. This slurry drains out laterally and is recirculated independently of the FDS slurry circuit. By this means, the initial scrubbing action in the FDS eliminates particulates, while the absorber slurry, high in absorbent content, effectively removes SO_2. The scrubbed gas passes through a 2 percent stage demister, leaves the absorber tower, and after passage through a steam reheater enters the stack.

The FDS slurry from the foot of each scrubber tower is pumped to an agitated FDS slurry tank, from which it is recirculated to the FDS. Similarly, the absorber slurries are collected in an absorber tower feed tank, where the limestone slurry required to replenish the reactant is added. Process makeup water is added to both the FDS slurry tank and the absorber tower feed tank, while a crossover line provides a bleedoff from the absorber tower slurry to the FDS slurry and, at the same time, provides the pH control for the FDS circuit by introducing limestone from the absorber tower feed.

A bleedoff line from the FDS slurry tank carries the sulfur waste product, a calcium sulfite-sulfate sludge, and fly ash to the disposal pond. This bleed is also used to slough mechanically collected fly ash to the disposal pond.

Sample sets were collected from the APS Cholla station on two occasions. The operating conditions and sampling locations representing each sampling occasion are presented in Table B-6. Sample locations are also indicated in Figure B-9. Samples C2 and C3 were collected in duplicate on the first occasion. One sample was filtered immediately upon collection; the other sample retained liquor and solids in contact until they were prepared for chemical analysis.


COAL
BOILER
FLUE GAS
REHEATER
STACK
BOOSTER FAN
DEMISTER SPRAY WASH
PACKED ABSORPTION TOWER AND CYCLONIC DEMISTER (See Figure B-10 for details)
FLOODED DISC SCRUBBER (FDS)
LIMESTONE
MAKEUP WATER
LIMESTONE SLURRY
TO ASH DISPOSAL POND
FDS SLURRY TANK
ABSORPTION TOWER FEED TANK

CIRCLED NUMBERS INDICATE SAMPLING LOCATIONS

Figure B-9. Schematic process diagram of the APS Cholla station FDS and packed absorption tower showing sampling locations.

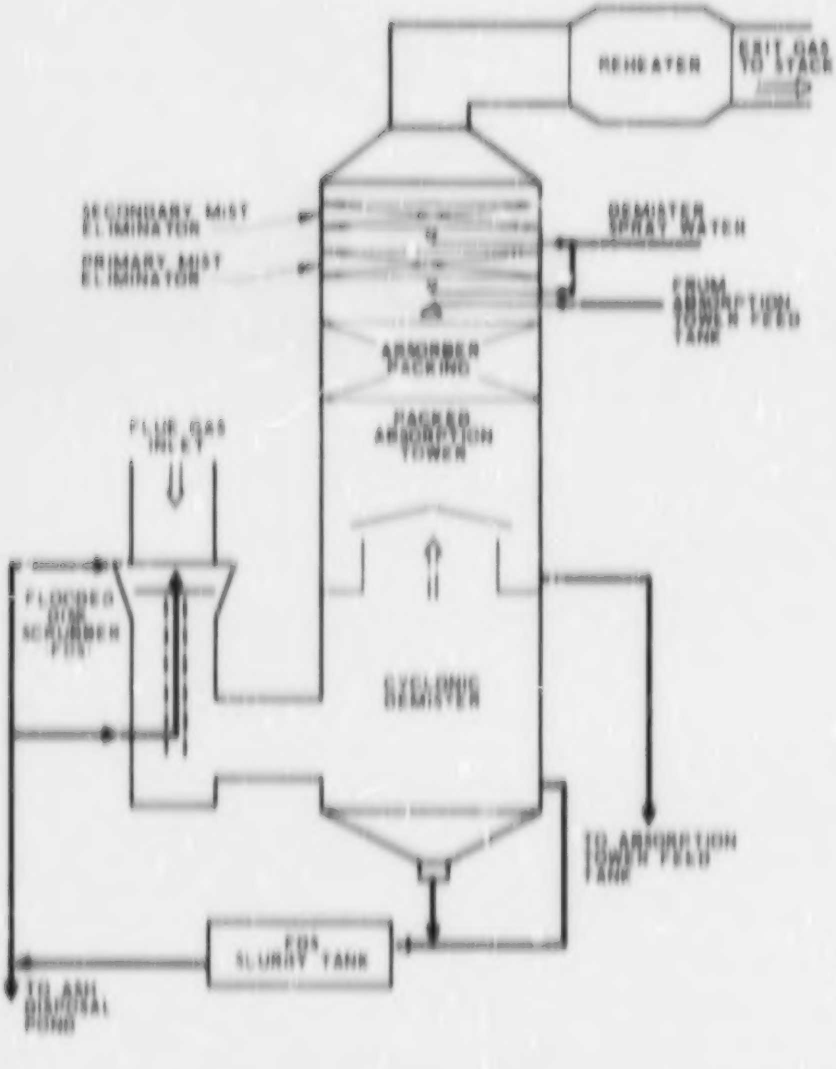

REHEATER
EXIT GAS TO STACK
SECONDARY MIST ELIMINATOR
DEMISTER SPRAY WATER
PRIMARY MIST ELIMINATOR
FROM ABSORPTION TOWER FEED TANK
ABSORBER PACKING
PACKED ABSORPTION TOWER
FLUE GAS INLET
FLOODED DISC SCRUBBER FDS
CYCLONIC DEMISTER
TO ABSORPTION TOWER FEED TANK
FDS SLURRY TANK
TO ASH DISPOSAL POND

Figure B-10. Schematic of APS Cholla station FDS and packed absorption tower scrubber.

TABLE E-6. APS CHOLLA SCRUBBER SYSTEM OPERATING CONDITIONS AND SAMPLE LOCATIONS

Operating Condition	1 Apr 1974	7 Nov 1974
Coal, % sulfur	0.5	0.5
Gas Flow Rate,		
m^3 sec^{-1}	151	151
ACFM	320,000	320,000
Equivalent Power, MW	115	115
SO_2 Input, ppm	360	360
SO_2 Removal, %	75	75
pH Control, Absorber Tower Circuit	6.5	6.5
Dust Input,		
g $(m)^{-3}$	0.41	0.41
gr $(scf)^{-1}$	0.18	0.18
FDS Slurry Tank Effluent, solids %	15	15
Absorber Tower Effluent, solids %	15	15
Liquid-to-Gas Ratio,		
gpm $(1000\ cfm)^{-1}$	70.9	70.8

Sample Location	1 Apr 1974	7 Nov 1974
Process Makeup Water	C1	C1
FDS Slurry Tank	C2	C2
Absorption Tower Effluent	C3	C3
Coal	C4	
Fly Ash	C5	
Limestone	C6	

B.5 GENERAL MOTORS (GM) CORPORATION PARMA POWER STATION DOUBLE-ALKALI SCRUBBER SYSTEM

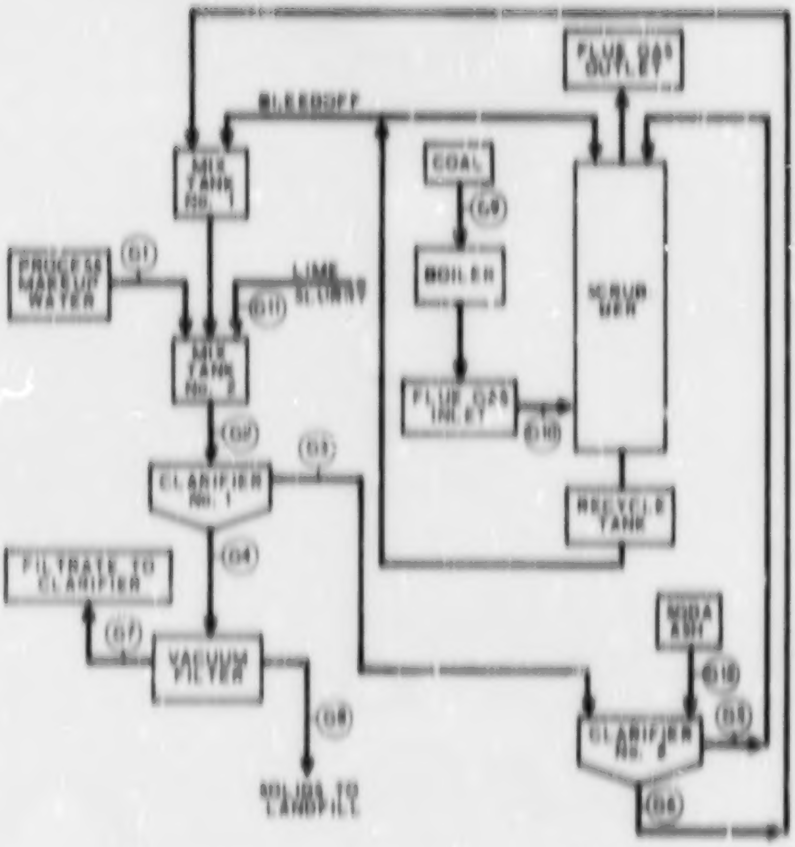
The GM double-alkali system is unique among the scrubber systems investigated in this report in that it removes SO_2 by a regenerable absorbent. The installation consists of four parallel Koch valve tray scrubber modules which remove SO_2 from the flue gas on the 32-MW industrial boilers at the GM Parma plant. Figure B-11 shows schematically one scrubber module in the scrubbing system.

Each scrubber consists of a vertical tower fitted with a series of three bubble-cap trays. Flue gas, cleaned of particulates by a mechanical fly ash remover, enters the bottom of the scrubber and passes upward through the tray orifices in a flow that is countercurrent to the descending sodium hydroxide scrubbing liquor. This liquor passes out through a bottom drain and is recirculated to the scrubber via a recycle tank.

For the recirculating liquor to be purged of its sulfite content, a bleedoff from the recycle tank discharge carries a portion of the liquor to mix tank no. 1 (neutralizer tank), where the weak acid liquor is blended with the alkaline clarifier no. 2 underflow. The liquor passes to mix tank no. 2 (recausticizer), where it is treated with a lime slurry, regenerating sodium hydroxide and producing a calcium sulfite precipitate. This is also the point in the system where a portion of the process makeup water is added, as a replacement for the water lost in the filter cake and hot stack gas. The underflow becomes the feed stream to clarifier no. 1, where the solid and liquor portions are separated. The underflow from clarifier no. 1, a thickened slurry high in calcium sulfite, goes to the vacuum filter for dewatering. The overflow contains calcium hydroxide in solution and is passed to clarifier no. 2 where the calcium ions react with soda ash (sodium carbonate) precipitating calcium carbonate and preventing the subsequent deposition of a calcium sulfate scale in the scrubber. The high carbonate concentration in this clarifier depresses the calcium content of the liquor, and fresh soda ash replaces the sodium lost in the filter cake. The clarifier no. 2 overflow is recirculated to the scrubber; the underflow, a sodium-calcium carbonate slurry, goes to mix tank no. 1 as an alkalizer to commence the liquor regeneration process.

The vacuum filter receives the slurry underflow from clarifier no. 1 and produces a clear filtrate, which is returned to the clarifiers. The filter cake is washed and refiltered before being trucked to a landfill area for disposal.

A single sample set was collected by GM personnel and delivered to The Aerospace Corporation for analysis. The scrubber system operating conditions and description of sample locations shown in Figure B-11 are presented in Table B-7.


FLUE GAS OUTLET
BLEEDOFF
COAL
MIX TANK NO. 1
(G9)
PROCESS MAKEUP WATER
(G1)
LIME SLURRY
(G11)
BOILER
SCRUBBER
MIX TANK NO. 2
FLUE GAS INLET
(G10)
(G2)
(G3)
CLARIFIER NO. 1
RECYCLE TANK
(G4)
FILTRATE TO CLARIFIER
SODA ASH
(G7)
VACUUM FILTER
(G12)
(G5)
(G8)
CLARIFIER NO. 2
SOLIDS TO LANDFILL
(G6)

CIRCLED NUMBERS INDICATE SAMPLING LOCATIONS

Figure B-11. Schematic process diagram of the GM scrubber system showing sampling locations.

TABLE B-7. GM DOUBLE-ALKALI SCRUBBER SYSTEM OPERATING CONDITIONS AND SAMPLE LOCATIONS

Operating Condition	18 Jul 1974
Coal, % sulfur	2.5
Gas Flow Rate Scrubber,	
$m^3 \, sec^{-1}$	13.3
ACFM	28,000
Equivalent Power, MW	12
SO_2 Input, ppm	1,300
SO_2 Removal, %	90
pH Control,	
Scrubber Recycle Liquor	6.0
Clarifier Return to Scrubber	12
Dust Input,	
$g \, (m)^{-3}$	0.7
$gr \, (scf)^{-1}$	0.3
Filter Cake, solids %	50
Liquid-to-Gas Ratio, $gpm \, (1000 \, cfm)^{-1}$	20

Sampling Location	18 Jul 1974
Process Makeup Water	G1
Mix Tank No. 2 Underflow	G2
Clarifier No. 1 Overflow	G3
Clarifier No. 1 Underflow	G4
Clarifier No. 2 Overflow	G5
Clarifier No. 2 Underflow	G6
Filter Filtrate	G7
Filter Cake	G8
Coal	G9
Fly Ash	G10
Lime	G11

B.6 UTAH POWER AND LIGHT (UPL) COMPANY GADSBY STATION ENVIROTECH DOUBLE-ALKALI SCRUBBING SYSTEM

The Envirotech scrubber system is a pilot plant installed in a 100-MW coal-fired boiler that scrubs flue gas from an equivalent of approximately 1-MW generating capacity. The system is a regenerating system using soda ash and lime as absorbents and is shown in Figure B-12. The scrubbing of the flue gas is done in two stages: the first stage is a venturi-cyclone separator scrubber; it is followed by a two-tray mobile bed scrubber as the second stage.

Flue gas enters the scrubbers after passing through mechanical and electrostatic precipitators and passes down through the venturi countercurrent to the scrubber liquor as it passes upward through the mobile bed scrubber. The flue gas then passes through a mist eliminator and is exhausted.

Scrubber liquor drains from the bottom of the scrubber into an oxidation tank, which serves also as a hold tank for the scrubber recirculation system. The bleed from the oxidation tank is pumped to a reaction tank where the alkaline underflow from reactor clarifier no. 2 is added for initial neutralization. The liquor passes then to a second reaction tank where slaked lime is added for further pH adjustment. The liquor is then passed to reactor clarifier no. 1, where the initial separation of solids and liquid takes place. The overflow passes to reactor clarifier no. 2, where soda ash is added as a softening step. The underflow from reactor clarifier no. 2 goes to the first reaction tank; the overflow returns to the oxidation tank. The underflow from reactor clarifier no. 1 is pumped to a thickener for further solids and liquid separation. The underflow from the thickener is passed to a vacuum filter; the filtrate is returned to the system; and the filter cake is discharged as a waste.

A single sample set was taken by Envirotech personnel for this study. The scrubber operating conditions and description of sample locations are shown in Table B-8 and Figure B-12.

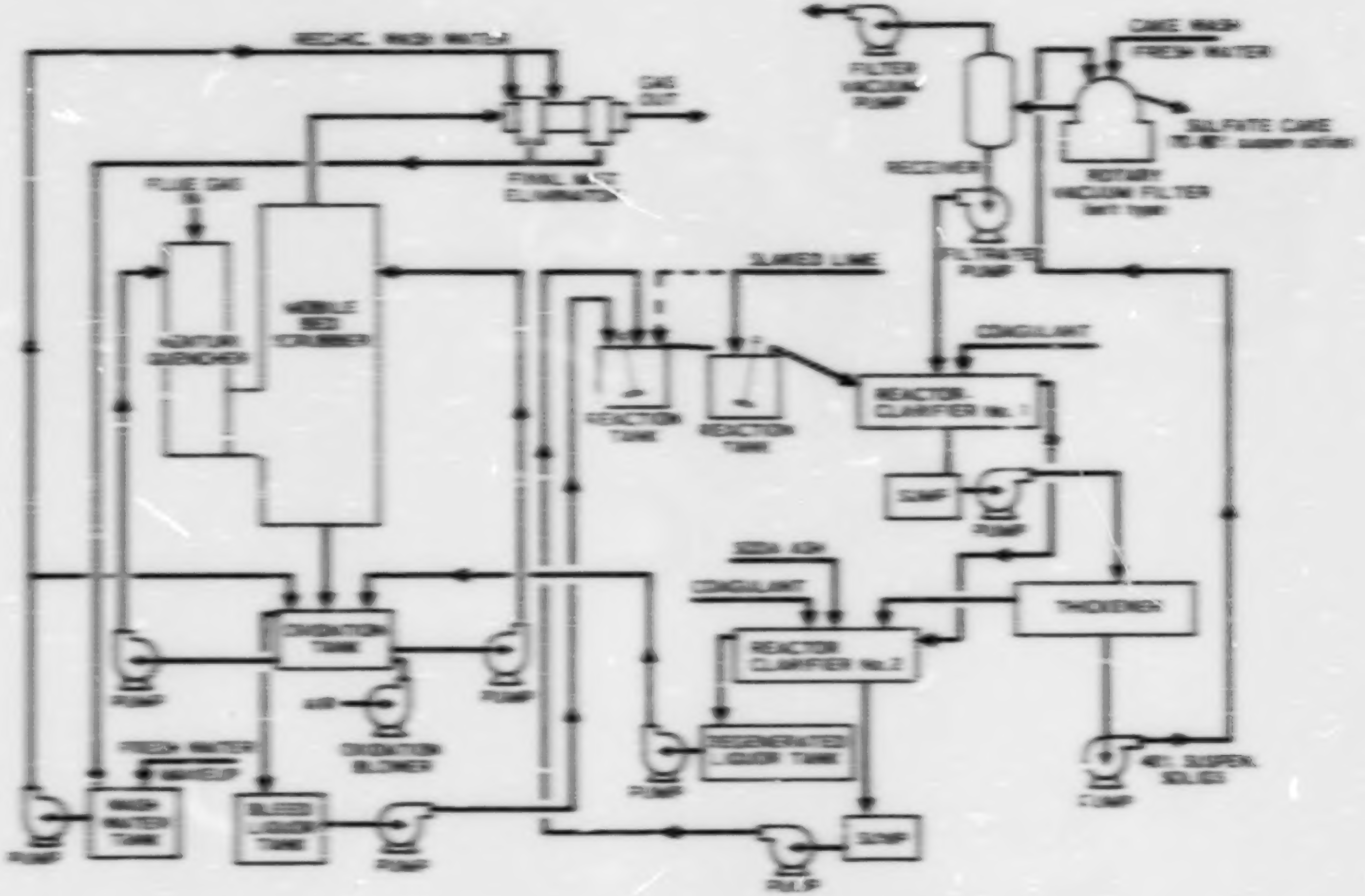

RECIRC. WASH WATER
GAS OUT
FINAL MIST ELIMINATOR
FLUE GAS IN
VENTURI QUENCHER
MOBILE BED SCRUBBER
OXIDATION TANK
PUMP
PUMP
AIR
OXIDATION BLOWER
FRESH WATER MAKEUP
PUMP
WASH WATER TANK
BLEED LIQUOR TANK
PUMP
REACTION TANK
REACTION TANK
SLAKED LIME
REACTOR-CLARIFIER No. 1
COAGULANT
SUMP
PUMP
SODA ASH
COAGULANT
REACTOR-CLARIFIER No. 2
THICKENER
PUMP
REGENERATED LIQUOR TANK
SUMP
PUMP
PUMP
40% SUSPEN. SOLIDS
FILTER VACUUM PUMP
RECEIVER
FILTRATE PUMP
CAKE WASH FRESH WATER
SULFITE CAKE
ROTARY VACUUM FILTER

Figure B-12. Schematic process diagram of the UPL Envirotech sulfate-mode double-alkali scrubber system.

TABLE B-8. UPL ENVIROTECH DOUBLE-ALKALI SCRUBBER SYSTEM OPERATING CONDITIONS AND SAMPLE LOCATIONS

Operating Condition	9 Aug 1974
Coal, % sulfur	0.4
Gas Flow Rate,	
m^3 sec^{-1}	1.2
ACFM	2500
Equivalent Power, MW	0.8
SO_2 Input, ppm	800
SO_2 Removal, %	90
pH Control	6.5
Dust Input,	
g $(m)^{-3}$	0.6
gr $(scf)^{-1}$	0.25
Filter Cake, solids %	15
Liquid-to-Gas Ratio,	
gpm $(1000\ cfm)^{-1}$	20
Oxidation Rate, %	90

APPENDIX C

CHEMICAL ANALYSIS TECHNIQUES USED BY AEROSPACE

C.1 INTRODUCTION

This appendix describes the analytical techniques used to determine the concentration of constituents in the liquid portions of flue gas desulfurization (FGD) sludges.[*] The constituents present in the liquor are divided into the following: major chemical species (calcium, magnesium, sodium, sulfite, sulfate, and chloride), trace metal species, and additional chemical species. Other water quality tests are also described. Solids analyses differed from liquor analyses primarily by sample preparation methods.

The precision and accuracy chosen for the measurements were strongly influenced by the relative cost of the analysis and the relative significance of the resultant value. The data obtained have as high a precision and accuracy as was considered warranted.[†] Although the basis for selecting the proper analytical technique was to minimize any interference from other species, the presence of chemical species interfering with a particular analysis was fully acknowledged. Only when the interference was considered significant were corrections applied.

C.2 MAJOR CHEMICAL SPECIES

C.2.1 Calcium Determination

The method selected for calcium determination has an accuracy of 4 percent. Calcium oxalate was precipitated and filtered from the solution; the filter cake was redissolved in HCl; and the solution was titrated against $KMnO_4$ to the characteristic purple end point. Correction was then made for excess permanganate.

An alternative technique of atomic absorption spectrophotometry was used for calcium analyses. Results for solutions analyzed by both methods demonstrated comparable agreement, to within 6 percent. At concentrations greater than 1000 mg/ℓ, the precision of each method was 3 to

---

[*] The methods defined in (20) and (21) were used wherever they were applicable to the requirements of the analyses.

[†] Precision is defined as the relationship between a measured value and the statistical mean of measured values, and accuracy is the relationship between the true value and the measured value.

5 percent, but at lower calcium concentrations the data spread in the oxalate method is greater than that of the spectrophotometric method. Atomic absorption will be used for all future analyses.

C.2.2 Magnesium Determination

Magnesium was determined by atomic absorption spectrophotometry to an accuracy and precision ranging between 3 and 5 percent.

C.2.3 Sodium Determination

Atomic absorption spectrophotometry or flame emission photometry was used to determine sodium ion concentrations, depending on whether the concentrations were relatively low or high. Total errors were generally less than 10 percent and typically less than 5 percent.

C.2.4 Sulfite Determination

Total sulfite was determined by use of a specific ion electrode, and no significant interferences were observed. The oxidation of the sulfite ion to sulfate in the scrubber liquor was found to be a rapid reaction. Liquor protected from the atmosphere typically reveals concentrations of several hundred milligrams per liter of the sulfite ion; however, a brief atmospheric exposure causes oxidation and reduces these concentrations by one or more orders of magnitude. The reported sulfite measurements were for samples analyzed immediately upon arrival in the laboratory. No specific action was taken to inhibit oxidation other than to ensure that the samples were transported from the power plant scrubber to the analytical laboratory in sealed containers. The exposure to air during sampling, filtering, and measuring, however, resulted in the sulfite values reported. It is presumed that these concentrations would probably more closely represent the oxidation state of liquors in the event of their potential discharge.

No value of accuracy or precision can be reported because of the relative instability of the sulfite ion. At concentrations greater than approximately 100 mg/ℓ, the iodine titration method is preferred. At concentrations below this value, the titration method is not applicable, and only the specific ion electrode can be used. Accuracy of 3 percent and precision of less than 5 percent were determined against sodium sulfite at approximately 50 mg/ℓ. For the lower concentrations, the titrimetric technique cannot be validated against the specific ion method.

C.2.5 Sulfate Determination

Standard nephelometry techniques were used for this analysis. A barium sulfate precipitate was formed by the reaction of the sulfate ion with a barium chloranilate reagent. The resulting turbidity was determined by a spectrophotometer and compared to a curve from standard sulfate solutions. Although multiple dilutions are necessary to bring the concentration to a range of optimum reliability, the resulting error is less than 10 percent.

C.2.6 Chloride Determination

A specific ion electrode was used to determine the concentration of chloride ions. Comparisons were made with results of titrations with silver nitrate. Two titrimetric methods of chloride analysis were conducted, and the results have been compared with the results of ion selective electrode measurements of chloride concentration. Titrations with silver nitrate were made, with chromate ion as the end-point detection (Mohr method), and these results were compared with potentiometric titrations. Both titration methods gave precisions within 1 percent, and the results of both methods agreed to approximately 1 percent. The precision of the ion selective electrode measurements was approximately ±5 percent, and the results of the titration methods of the same solutions with $AgNO_3$ were well within the uncertainty band of the electrode measurements. The chloride concentrations of these samples were between 2000 and 4000 mg/ℓ. At much lower chloride concentrations, the ion selective electrode method has an advantage because the precision of the electrode measurement is not appreciably affected by the concentration level, in contrast to either of the titrimetric methods for which the precision decreases at lower concentration values.

C.3 TRACE ELEMENT SPECIES

Since most trace element species are highly sensitive to atomic absorption spectrophotometry, the flameless technique was used for the following elements: aluminum, beryllium, cadmium, chromium, copper, lead, and zinc. Results were verified by the National Bureau of Standards (NBS) analysis standards and by comparative analyses of elements present in relatively high concentrations by means of gravimetric or volumetric methods. Precision and accuracy are dependent upon the means of activation, the specific element, its relative concentration, and the extent of interference by other elements and matrix effects. The precision and accuracy of the measurements at concentrations of all of these elements between 1.0 and 0.010 mg/ℓ ranged between 5 and 50 percent. However, with furnace activation, the precision of trace elements occurring at even lower concentration levels decreases as the detection limit is approached.

Mercury was also determined by this technique; however, the mercury was reduced to the elemental state with stannous chloride, and the absorption of the resulting mercury vapor was measured. This method has a precision of about 20 percent and an accuracy of about 20 percent in the range 0.005 to 0.0005 mg/ℓ.

Arsenic was determined by reacting arsine with mercurous bromide to produce Hg_3As; the unknown was compared colorimetrically against standards. For this application, this technique has a precision of about 25 percent and an accuracy of about 25 percent in the range 0.10 to 0.01 mg/ℓ.

A fluorimetric technique that has a sensitivity within 1 mg/ℓ was used to determine selenium. It has a precision of about 10 percent and an accuracy of 60 percent between 0.20 to 0.02 mg/ℓ.

Plans to change the arsenic and selenium analyses to atomic absorption spectrophotometry are being implemented.

C.4 ADDITIONAL CHEMICAL SPECIES

C.4.1 Potassium Determination

Potassium was determined by the same techniques as sodium; and the precision and accuracy obtained were generally betwenn 3 to 5 percent.

C.4.2 FLUORIDE DETERMINATION

The fluoride ion was determined by the specific ion electrode using a Beckman Model 4560 digital pH meter. There were no significant interferences in the scrubber liquors. This method has a precision of about 5 percent; an accuracy of 20 percent is attainable at the low levels measured. For future analyses, a Bellack distillation will be performed prior to specific electrode measurements.

C.5 OTHER WATER QUALITY TESTS

C.5.1 pH Determination

This parameter was measured with a Beckman Model 4500 digital pH meter to a precision of 0.002 pH units and an accuracy of 0.005 pH units.

C.5.2 Total Dissolved Solids (TDS) Determination

The TDS were determined gravimetrically by evaporating a 25-ml sample overnight in a tared weighing bottle, under vacuum at 120°F. Since two of the major constituents (calcium and sodium sulfates) form stable hydrated salts and are hygroscopic in the anhydrous state, prolonged drying and minimal exposure of the dried residue were mandatory. This method has a precision of about 2 percent, and an accuracy of about 5 percent.

C.6 ANALYTICAL METHODS APPLICABLE TO SLUDGE SOLIDS

Sludge solids were analyzed for calcium, sulfate, sulfite, and carbonate, as well as total solids and inert material (fly ash).

Calcium was determined by a volumetric method, following an oxalate separation. The sample, commonly 0.25 g, was dissolved in hydrochloric and nitric acids, diluted, and filtered, and calcium oxalate was precipitated by ammonium oxalate from a slightly alkaline solution. The precipitate was filtered off, redissolved in sulfuric acid, and titrated with standard potassium permanganate.

Sulfate was determined gravimetrically, taking a 0.25-g sample which was dissolved in hydrochloric acid. The solution was filtered, and barium chloride added to the hot filtrate to precipitate barium sulfate. This was filtered off through a tared Gooch crucible with a glass filter pad. It was then dried and ignited at 800°C, cooled, and weighed.

Sulfite was determined volumetrically. A 2-g sample was placed in a three-necked flask, fitted with a dropping funnel for adding sulfuric acid, an entrance tube for nitrogen used to sweep out the evolved gases, and an exit tube dipping into an absorbent solution of 1/10 nitrogen-sodium hydroxide. After SO_2 was evolved and collected as sodium sulfite, the excess sodium hydroxide was neutralized and the sulfite titrated with standard iodine.

Carbonate was determined by a gravimetric method after evolution as CO_2, along with SO_2, by acidifying a 2-g sample in a tared flask. The flask was warmed gently to expel all gases, cooled, and weighed. The weight decrease represents $CO_2 + SO_2$ and must be corrected for the SO_2 content as determined volumetrically.

APPENDIX D

CHEMICAL CHARACTERIZATION DATA SHEETS

The following tables present the results of the chemical analyses performed on the liquid and solid portions of flue gas desulfurization (FGD) sludge samples taken at various locations within the waste streams of FGD scrubbing systems. The concentration values, as presented, represent either the mean or median of a minimum of three and a possible maximum of nine independent measurements. Three independent commercial laboratories were used to supplement the in-house analyses. Data acceptance was made only after the results of two (and sometimes three) independent analyses were evaluated. (Each analysis is the mean of three separate measurements.)

A description of the scrubbing facilities is given in Appendix B, and a description of the analytical methods is given in Appendix C. An evaluation of these data is presented in Section 7.3.1, and detailed discussions of the relationship of these data to system parameters are presented in Section 7.4.

Tables D-1 through D-13 present results from chemical analyses of the liquid samples from various locations within the scrubbing systems, as defined in Appendix B, Tables B-1 through B-6. Tables D-14 through D-17 are summation tables for four of the scrubbing systems, giving more extensive analytical results. Table D-18 through D-27 are analyses of solids from these scrubber systems, also defined in Tables B-1 through B-6.

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TABLE D-1. ANALYSIS OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT

Date: 1 Feb 1973
Conc: mg/ℓ

TCA Scrubber-Limestone System

Scrubber Liquor Constituents	Sampling Locations			
	Process Makeup Water	Scrubber Effluent (Separated)	Scrubber Effluent (Retained)	Clarifier Effluent (Retained)
Aluminum		1.7	0.7	0.2
Arsenic	< 0.2	1.2	0.8	1.7
Beryllium	< 0.0005	0.006	0.015	0.012
Cadmium	< 0.0005	0.009	0.001	0.004
Calcium		1800	1600	860
Chromium	< 0.001	0.025	0.006	0.015
Copper	0.012	0.041	0.021	0.051
Lead	< 0.005	0.030	0.026	0.039
Magnesium		100	53	42
Mercury	0.007	-	-	-
Potassium	-	-	24	28
Selenium	< 0.01	0.35	0.15	0.54
Sodium	-	-	12	10
Zinc	< 0.2	4	10	11
Chloride	-	-	1000	900
Fluoride	-	-	-	3.4
Sulfate	-	-	2500	1280
Sulfite	-	460	160	180
TDS	-	5800	5400	3200
pH	7.4	2.3	7.8	7.2

Dash indicates sample not analyzed or insufficient sample.

TABLE D-2. ANALYSIS OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT

Date: 12 Jul 1973

Conc: mg/ℓ

TCA Scrubber-Limestone System

Scrubber Liquor Constituents	Sampling Locations			
	Process Makeup Water	Scrubber Effluent (Separated)	Scrubber Effluent (Retained)	Clarifier Effluent (Retained)
Aluminum	0.04	1.5	0.5	0.3
Arsenic	0.02	2.0	2.0	1.8
Beryllium	0.0012	0.020	0.028	0.026
Cadmium	0.0005	0.0072	0.0092	0.0089
Calcium	-	2200	3100	2600
Chromium	0.001	0.13	0.17	0.20
Copper	0.005	0.060	0.064	0.052
Lead	0.005	0.19	0.32	0.28
Magnesium	-	100	50	160
Mercury	0.0001	0.11	0.14	0.04
Potassium	-	-	37	43
Selenium	0.01	2.0	3.1	2.7
Sodium	-	-	80	87
Zinc	0.4	29	38	27
Chloride	20	4800	6000	5000
Fluoride	1.2	0.4	0.25	3.1
Sulfate	-	-	2100	1800
Sulfite	-	-	110	90
TDS			11,500	10,200
pH	7.3	2.44	8.4	9.01

Dash indicates sample not analyzed or insufficient sample.

TABLE D-3. ANALYSIS OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT

Date: 27 Nov 1973

Conc: mg/ℓ

TCA Scrubber-Limestone System

Scrubber Liquor Constituents	Sampling Locations			
	Process Makeup Water	Scrubber Effluent (Separated)	Scrubber Effluent (Retained)	Clarifier Effluent (Retained)
Aluminum	-	-	-	-
Arsenic	≤ 0.001	0.14	0.31	0.28
Beryllium	-	0.01	0.01	0.004
Cadmium	-	0.04	0.013	0.004
Calcium	-	1600	1800	1600
Chromium	-	0.040	0.12	0.91
Copper	-	0.05	0.45	0.41
Lead	0.0005	0.006	0.06	0.12
Magnesium	-	-	900	600
Mercury	-	-	-	0.05
Potassium	-	6.3	5.4	5.9
Selenium	-	0.2	0.2	0.2
Sodium	-	63	67	69
Zinc	0.13	0.84	0.62	0.35
Chloride	-	3100	3700	3100
Fluoride	-	2.3	2.0	2.4
Sulfate	-	2400	3000	2100
Sulfite	-	1.7	3.0	2.1
TDS	-	8500	12,000	11,000
pH	-	6.7	5.9	9.6

Dash indicates sample not analyzed or insufficient sample.

TABLE D-4. ANALYSIS OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT

Date: 15 Jun 1974

Conc. mg/ℓ

TCA Scrubber-Limestone System

Scrubber Liquor Constituents	Sampling Locations				
	Process Makeup Water	Scrubber Effluent (Separated)	Scrubber Effluent (Retained)	Clarifier Effluent (Separated)	Clarifier Effluent (Retained)
Aluminum	-	-	2,7	-	0,6
Arsenic	0,004	0,39	0,39	0,13	0,14
Beryllium	0,004	0,069	0,074	0,052	0,054
Cadmium	0,005	0.006	0,004	0,004	0,003
Calcium	-	660	840	520	600
Chromium	0,002	0,16	0,13	0,09	0,09
Copper	0,01	0,02	0,02	0,01	0,01
Lead	0,006	0,35	0,30	0,21	0,25
Magnesium	-	2800	2800	2600	2750
Mercury	<0,05	<0,05	<0,05	<0,05	<0,05
Potassium	-	-	-	32	41
Selenium	-	<0,2	0,08	0,1	<0,2
Sodium	-	-	-	76	79
Zinc	-	0,04	0,03	0,03	0,02
Chloride	-	3700	3300	2300	2250
Fluoride	-	2,1	2,2	6,5	6,2
Sulfate	-	9000	10,000	10,000	9800
Sulfite	-	1550	1150	55	110
TDS		16,500	17,800	15,000	15,900
pH	7,1	4,6	5,5	8,0	8,3

Dash indicates sample not analysed or insufficient sample.

TABLE D-5. ANALYSIS OF SCRUBBER LIQUOR FROM SCE MOHAVE GENERATING STATION

Date: 30 Mar 1973

Conc: mg/ℓ

TCA Scrubber-Limestone System

Scrubber Liquor Constituents	Sampling Locations			
	Process Makeup Water	Scrubber Effluent	Scrubber Recirculation	Centrifuge Effluent
Aluminum	-	-	0,04	-
Arsenic	0,01	0,03	0,038	0,028
Beryllium	0,011	0,03	0,03	0,02
Cadmium	0,07	0,05	0,05	0,05
Calcium	610	200	300	180
Chromium	0,03	0,23	0,3	0,25
Copper	-	0,08	0,2	0,56
Lead	0,003	0,06	0,11	0,04
Magnesium	230	310	300	390
Mercury	≤0,05	0,0012	0,00057	≤0,005
Potassium	130	100	100	100
Selenium	≤0,0005	0,12	0,11	0,1
Sodium	2700	30,000	29,000	29,000
Zinc	-	0,12	0,18	0.18
Chloride	4050	30,600	28,000	33,000
Sulfate	2500	22,000	24,000	16,650
TDS	12,700	95,000	94,800	92,500
pH	9,1	7.8	7.5	6.7

Dash indicates sample not analyzed or insufficient sample.

TABLE D-6. ANALYSIS OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT

Date: 19 Mar 1974

Conc: mg/ℓ

Venturi-Spray Tower-Lime System

Scrubber Liquor Constituents	Sampling Locations						
	Process Makeup Water	Scrubber Effluent (Separated)	Scrubber Effluent (Retained)	Clarifier Effluent (Separated)	Clarifier Effluent (Retained)	Filter Effluent (Filtrate)	Lime Slurry
Aluminum	-	0.22	0.06	0.12	0.03	0.08	0.21
Arsenic	< 0.004	0.15	0.21	0.17	0.30	0.15	0.10
Beryllium	0.003	0.050	0. 0.023	0.020	0.027	0.076	0.004
Cadmium	-	0.03	0.01	0.02	0.03	0.03	0.01
Calcium	-	980	900	840	800	660	720
Chromium	0.004	0.07	0.03	0.01	0.02	0.03	0.01
Copper	0.01	0.08	0.10	0.04	0.07	0.05	0.02
Lead	0.03	0.03	[illegible].008	0.04	0.06	0.01	0.009
Magnesium	-	51	56	23	25	24	1
Mercury	0.001	0.10	0.04	0.09	0.07	0.07	0.07
Potassium	-	8.4	8.6	6.8	13	11	29
Selenium	0.003	0.08	0.10	0.08	0.03	0.05	0.08
Sodium	-	71	33	36	28	36	88
Zinc	0.03	0.09	0.07	0.02	0.01	0.01	0.01
Chloride	-	1230	1290	1210	1040	1050	720
Fluoride	-	< 0.1	< 0.1	1.4	1.4	1.4	40
Sulfate	-	1000	800	1350	1000	900	100
Sulfite	-	450	0.8	1.8	2.2	1.7	-
TDS	-	3500	3300	3500	3200	2800	1800
pH	7.8	5.2	5.4	9.5	9.0	9.4	12.7

Dash indicates sample not analyzed or insufficient sample

TABLE D-7. ANALYSIS OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT

Date: 16 May 1974

Conc: mg/l

Venturi-Spray Tower-Lime System

Scrubber Liquor Constituents	Sampling Locations				
	Scrubber Effluent (Separated)	Scrubber Effluent (Retained)	Clarifier Effluent (Separated)	Clarifier Effluent (Retained)	Filter Effluent (Filtrate)
Aluminum	0,12	0,5	0,5	0,3	0,1
Arsenic	0,15	0,04	0,06	0,03	0,01
Beryllium	0,05	0,04	0,20	0,07	0,05
Cadmium	0,04	0,006	0,004	0,004	0,013
Calcium	2360	2500	2340	2580	2420
Chromium	0,02	0,008	0,03	0,01	0,02
Copper	0,03	0,02	0,06	0,07	0,04
Lead	0,13	0,11	0,14	0,13	0,13
Magnesium	220	215	210	220	200
Mercury	<0,05	<0,05	<0,05	<0,05	<0,05
Potassium	21	24	30	29	27
Selenium	1,9	1,7	1,5	1,9	1,9
Sodium	108	165	108	104	109
Zinc	0,02	0,03	0,02	0,02	0,02
Chloride	4400	4400	4300	4200	4200
Fluoride	1,5	2,2	2,6	4,5	3,0
Sulfate	1500	1400	1350	1350	1250
Sulfite	3,0	1,8	4,6	2,3	2,7
TDS	8700	8200	8000	7800	8400
pH	5,6	7,0	8,4	9,1	8,8

Dash indicates sample not analyzed or insufficient sample.

TABLE D-8. ANALYSIS OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT

Date: 27 Jun 1974

Conc: mg/l

Venturi-Spray Tower-Lime System

Scrubber Liquor Constituents	Sampling Locations			
	Scrubber Effluent (Separated)	Scrubber Effluent (Retained)	Clarifier Effluent (Retained)	Filter Effluent (Filtrate)
Aluminum	1,54		≤ 0,1	0,24
Arsenic	0,04	≤0,01	0,02	0,02
Beryllium	≤0,002	≤0,002	≤ 0,002	≤ 0,002
Cadmium	0,12	0,12	0,11	0,11
Calcium	3000	3060	2820	2520
Chromium	0,04	0,04	0,04	0,03
Copper	0,01	0,005	< 0,002	0,002
Lead	0,33	0,37	0,39	0,33
Magnesium	420	410	450	420
Mercury	≤0,001	≤ 0,001	≤ 0,001	≤ 0,001
Potassium	25	27	32	28
Selenium	≤ 0,02	≤ 0,02	≤ 0,02	≤ 0,02
Sodium	126	122	125	127
Zinc	0,18	0,14	0,11	0,08
Chloride	5800	5200	5900	4900
Fluoride	0,2	0,9	4,0	3,3
Sulfate	800	700	800	800
Sulfite	12	≤ 0,6	0,8	0,9
TDS	10,800	10,000	10,400	9400
pH	2,7	5,4	9,0	8,7

TABLE D-9. ANALYSIS OF SCRUBBER LIQUORS FROM APS CHOLLA POWER PLANT

Date: 1 April 1974
Conc: mg/ℓ

Venturi-Absorber-Limestone System

Scrubber Liquor Constituents	Sampling Locations			
	Process Makeup Water	Slurry Tank (Separated)	Slurry Tank (Retained)	Absorbent Tower Effluent
Aluminum	-	2	2	0.6
Arsenic	<0.004	<0.004	<0.004	<0.004
Beryllium	0.10	0.14	0.18	0.08
Cadmium	0.08	0.011	0.009	0.007
Calcium	140	680	700	590
Chromium	0.02	0.14	0.21	0.02
Copper	0.04	0.20	0.19	0.03
Lead	0.004	0.01	0.01	0.07
Magnesium	5.8	3	6	7
Mercury	0.04	0.07	0.13	0.007
Potassium	-	14	16	-
Selenium	1.2	2.2	2.5	1.0
Sodium	-	2150	2250	800
Zinc	0.05	0.11	0.07	0.02
Chloride	-	1700	1430	620
Fluoride	-	0.7	0.6	2.4
Sulfate	300	4000	4000	2200
Sulfite	<1	0.9	<1	1
TDS	-	8700	9100	4300
pH	-	3.04	4.3	6.6

Dash indicates sample not analyzed or insufficient sample.

TABLE D-10. ANALYSIS OF SCRUBBER LIQUORS FROM APS CHOLLA POWER PLANT

Date: 7 Nov 1974
Conc: mg/ℓ

Venturi-Absorber-Limestone System

Scrubber Liquor Constituents	Sampling Locations			
	Process Makeup Water	Slurry Tank (Separated)	Absorbent Tower Effluent	
Aluminum	-	-	2,1	
Arsenic	≤0,004	-	0,02	
Beryllium	<0,003	0,038	≤0,003	
Cadmium	0,0065	0,044	0,012	
Calcium	27	770	390	
Chromium	≤0,004	0,024	0,004	
Copper	0,014	0,16	0,010	
Lead	0,07	0,37	0,15	
Magnesium	-	4	9	
Mercury	0,0015	<0,05	≤0,5	
Potassium	9	28	8	
Selenium	0,0006	<0,0006	0,033	
Sodium	570	1650	370	
Zinc	0,027	0,4,	0,036	
Chloride	940	4200	760	
Fluoride	1,1	1,5	1,0	
Sulfate	250	3750	1360	
Sulfite	2,5	3500	21	
TDS	2438	14,000	3300	
pH	8,4	3,4	6,8	

Dash indicates sample not analyzed or insufficient sample.

TABLE D-11. ANALYSIS OF SCRUBBER LIQUORS FROM DLC PHILLIPS STATION

Date: 4 Oct 1973

Conc: mg/ℓ

Venturi-Lime System

Scrubber Liquor Constituents	Sampling Locations		
	Process Makeup Water	Thickener Overflow	Thickener Underflow
Aluminum	-	-	-
Arsenic	<0.001	0.085	0.09
Beryllium	<0.0005	0.012	0.012
Cadmium	0.003	0.022	0.023
Calcium	50	1300	1400
Chromium	<0.001	0.017	0.040
Copper	0.003	0.06	0.07
Lead	0.0012	0.08	0.18
Magnesium	40	220	410
Mercury	0.003	0.09	0.05
Potassium	-	20	22
Selenium	<0.01	0.8	0.8
Sodium	-	1680	2400
Zinc	0.013	0.12	0.09
Chloride	-	1800	2700
Fluoride	-	4.8	2.6
Sulfate	-	4500	6450
Sulfite	-	<1	27
TDS	-	9400	14,000
pH		9.2	7.1

Dash indicates sample not analyzed or insufficient sample.

TABLE D-12. ANALYSIS OF SCRUBBER LIQUORS FROM DLC PHILLIPS STATION

Date: 17 Jun 1974
Conc: mg/ℓ

Venturi-Lime System

Scrubber Liquor Constituents	Sampling Locations				
	Process Makeup Water	Scrubber Effluent	Thickener Overflow	Thickener Underflow	Pond Sludge Liquid
Aluminum	-	-	-	-	-
Arsenic	<0,004	0,06	<0,004	≤0,004	<0,004
Beryllium	<0,0002	0,002	0,002	0,003	0,002
Cadmium	-	0,1	-	0,05	-
Calcium	-	660	680	600	600
Chromium	-	-	-	-	-
Copper	-	-	-	-	-
Lead	<0,006	0,05	0,06	<0,04	0,04
Magnesium	-	-	-	-	-
Mercury	0,0002	0,0004	0,0002	0,0002	0,0004
Potassium	-	10	2,6	2,6	22
Selenium	0,005	0,33	0,20	0,028	0,095
Sodium	-	440	380	320	340
Zinc	-	-	-	-	-
Chloride	-	540	350	470	420
Fluoride	-	8	2	10	7
Sulfate		2700	2800	2720	1000
Sulfite	-	1,7	0,8	20	4,8
TDS	-	4600	4400	4200	4000
pH	-	8,9	4,1	10,7	10,4

TABLE D-13. ANALYSIS OF SCRUBBER LIQUORS FOR GM UTILITY BOILER

Date: 18 Jul 1974
Conc: mg/ℓ

Bubble Cap Tray-Double Alkali System

Scrubber Liquor Constituents	Sampling Locations						
	Process Makeup Water	Mix Tank No. 2 Underflow	Clarifier No. 1 Overflow	Clarifier No. 1 Underflow	Clarifier No. 2 Overflow	Clarifier No. 2 Underflow	Filter Effluent (Filtrate)
Aluminum	-	-	-	-	-	-	-
Arsenic	< 0.004	< 0.004	< 0.004	-	< 0.004	< 0.004	< 0.004
Beryllium	< 0.002	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Cadmium	< 0.005	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Calcium	-	420	640	640	290	300	470
Chromium	< 0.003	< 0.03	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Copper	< 0.005	0.06	0.02	0.06	0.05	0.06	0.06
Lead	< 0.02	0.42	0.56	0.55	0.55	0.33	0.52
Magnesium							
Mercury	0.0004	0.002	< 0.0002	0.0009	0.0002	0.0014	0.005
Potassium	-	95	140	110	120	160	-
Selenium	0.002	0.15	0.14	0.087	0.19	0.26	0.075
Sodium	-	-	-	20,000	20,000	-	20,000
Zinc	0.07	0.06	0.09	0.63	0.05	0.06	0.59
Chloride	-	3500	3700	4400	3100	4300	5200
Fluoride	-	58	96	82	92	46	58
Sulfate	-	25,000	34,000	30,000	33,000	30,000	35,000
Sulfite	-	400	250	160	340	260	140
TDS	-	51,000	67,000	55,000	62,000	68,000	65,000
pH		12.6	12.6	12.8	12.5	12.5	12.7

Dash indicates sample not analyzed or insufficient sample

TABLE B-14. ANALYSES OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT: TCA SCRUBBER SYSTEM

(Scrubber test conditions at time of sampling shown in Table B-3)

Scrubber liquor constituents[a]	In-process data		Potential discharge point data	
	Sample location			
	Scrubber effluent		Clarifier underflow	
	Sample date			
	11/27/73	6/13/74	11/27/73	6/13/74
Aluminum (Al)	--	2.7	--	0.6
Antimony (Sb)	--	2.0	--	1.4
Arsenic (As)	0.2	0.4	0.1	0.1
Beryllium (Be)	0.01	0.07	0.004	0.01
Boron (B)	--	--	--	--
Cadmium (Cd)	0.04	0.005	0.004	0.004
Calcium (Ca)	1800	840	1600	520
Chromium (Cr) (total)	0.04	0.16	0.5	0.09
Cobalt (Co)	--	0.16	--	0.10
Copper (Cu)	0.05	0.02	0.4	0.01
Iron (Fe)	--	0.35	--	0.02
Lead (Pb)	0.06	0.15	0.12	0.23
Magnesium (Mg)	900	2800	600	2750
Manganese (Mn)	--	--	--	--
Mercury (Hg)	--	<0.5	0.05	<0.05
Molybdenum (Mo)	--	--	--	--
Nickel (Ni)	0.16	0.44	0.50	0.33
Potassium (K)	6.1	--	5.9	41
Selenium (Se)	0.2	--	0.2	0.1
Silicon (Si)	--	--	--	--
Silver (Ag)	--	0.008	--	0.005
Sodium (Na)	63	--	59	--
Tin (Sn)	--	--	--	--
Vanadium (V)	--	--	--	--
Zinc (Zn)	0.84	0.03	0.31	0.02
Total carbonate	--	--	--	--
Chloride (Cl)	3400	3300	3100	2300
Fluoride (F)	2.3	2.1	2.4	5.5
Sulfite	--	1400	--	80
Sulfate	2700	9500	2100	10000
Phosphate	<0.1	<0.1	<0.1	<0.1
Total nitrogen	<0.005	<0.005	<0.005	<0.005
Chemical oxygen demand	--	--	--	--
Total dissolved solids	12000	17800	11000	17000
Total alkalinity	--	--	150	--
Conductance, mho/cm	--	0.027	--	0.015
Turbidity, Jackson units	<1	<1	<1	<1
pH	5.90	4.54	9.50	7.96

[a] Concentration in milligrams per liter unless otherwise indicated.

TABLE B-15. ANALYSES OF SCRUBBER LIQUORS FROM TVA SHAWNEE STEAM PLANT (VENTURI AND SPRAY TOWER SCRUBBER SYSTEM)

(Scrubber test conditions at time of sampling shown in Table B-2)

Scrubber liquor constituents[a]	In-process data			Potential discharge point data					
	Sample location								
	Scrubber effluent			Clarifier underflow			Drum vacuum filter filtrate		
	Sample date								
	3/19/74	5/16/74	6/27/74	3/19/74	5/16/74	6/27/74	3/19/74	5/16/74	6/27/74
Aluminum (Al)	0.22	0.14	1.58	0.03	0.1	<0.1	0.08	0.1	0.24
Antimony (Sb)	0.37	2.1	1.01	0.53	2.3	1.11	0.46	1.6	1.01
Arsenic (As)	0.15	0.15	0.04	0.10	0.03	0.02	0.13	0.01	0.02
Beryllium (Be)	0.05	0.05	<0.002	0.027	0.07	<0.002	0.026	0.05	<0.002
Boron (B)	[illegible]	[illegible]	36	[illegible]	[illegible]	46	[illegible]	[illegible]	41
Cadmium (Cd)	0.02	0.03	0.12	0.03	0.004	0.11	0.03	0.023	0.10
Calcium (Ca)	980	2360	1005	650	2380	2620	660	2370	2520
Chromium (Cr) (total)	0.02	0.02	0.08	0.02	0.01	0.08	0.03	0.02	0.03
Cobalt (Co)	[illegible]	0.6	0.31	[illegible]	0.6	0.42	[illegible]	0.7	0.33
Copper (Cu)	0.08	0.03	0.01	0.07	0.07	<0.002	0.05	0.04	<0.002
Iron (Fe)	0.77	0.18	1.81	0.08	0.27	0.10	0.02	0.10	0.06
Lead (Pb)	0.03	0.12	0.37	0.06	0.13	0.19	0.01	0.13	0.33
Magnesium (Mg)	33	220	420	25	220	450	24	200	420
Manganese (Mn)	[illegible]	0.4	[illegible]	[illegible]	0.09	0.46	[illegible]	0.2	0.14
Mercury (Hg)	0.10	<0.01	<0.001	0.07	<0.01	<0.001	0.07	<0.01	<0.001
Molybdenum (Mo)	[illegible]	[illegible]	6.1	[illegible]	[illegible]	6.1	[illegible]	[illegible]	5.1
Nickel (Ni)	0.2	0.21	0.29	0.08	0.21	0.24	0.03	0.34	0.21
Potassium (K)	8.4	21	25	11	25	32	11	27	28
Selenium (Se)	0.08	1.9	<0.02	0.03	1.9	<0.02	0.03	1.9	<0.02
Silicon (Si)	0.4	1.8	2.1	0.3	1.8	1.0	0.2	1.7	2.7
Silver (Ag)	0.03	0.01	0.03	0.06	0.01	0.03	0.06	0.03	0.02
Sodium (Na)	33	108	126	35	104	125	36	109	127
Tin (Sn)	[illegible]	[illegible]	3.5	[illegible]	[illegible]	3.5	[illegible]	[illegible]	3.1
Vanadium (V)	[illegible]	[illegible]	[illegible]	<0.001	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Zinc (Zn)	0.03	0.02	0.18	0.01	0.02	0.11	0.01	0.02	0.08
Total carbonate	<10	<10	<10	<10	<10	<10	<10	<10	<10
Chloride (Cl)	1410	4400	5400	1080	4200	5900	1050	4200	4900
Fluoride (F)	<0.3	1.5	0.2	1.4	4.3	4.0	1.3	1.0	3.3
Sulfite	450	1.0	12	2.2	2.3	0.8	1.7	2.7	0.9
Sulfate	1000	1500	1800	1000	1350	800	900	1250	800
Phosphate	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total nitrogen	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Chemical oxygen demand	220	[illegible]	149	160	[illegible]	98	83	[illegible]	83
Total dissolved solids	3300	8700	10800	3200	7800	10400	2800	8400	9800
Total alkalinity	58	[illegible]	61	45	[illegible]	82	57	[illegible]	76
Conductance, mho/cm	0.006	0.013	0.019	0.004	0.014	0.018	0.004	0.012	0.013
Turbidity, Jackson units	<1	<1	<1	<1	<1	<1	<10	<10	<10
pH	5.13	5.67	5.41	5.02	5.12	8.33	5.43	8.01	8.18

[a] Concentration in milligrams per liter unless otherwise indicated.

TABLE B-16. ANALYSES OF SCRUBBER LIQUORS FROM APS CHOLLA STATION (FDS AND ABSORPTION TOWER SCRUBBER SYSTEM)

(Scrubber test conditions at time of sampling shown in Table B-6)

Scrubber liquor constituents[a]	In-process data		Potential discharge data point	
	Sample location			
	Absorption tower tank		FDS tank	
	Sample date			
	4/1/74	11/7/74	4/1/74	11/7/74
Aluminum (Al)	0.06	2.1	2	<1
Antimony (Sb)	0.01	0.16	0.02	0.22
Arsenic (As)	<0.004	0.02	<0.004	<1
Beryllium (Be)	0.08	<0.001	0.14	0.04
Boron (B)	<1	1.8	<1	8.0
Cadmium (Cd)	0.007	0.012	0.011	0.044
Calcium (Ca)	580	190	680	770
Chromium (Cr) (total)	0.02	0.004	0.14	0.024
Cobalt (Co)	0.02	<0.01	0.17	0.1
Copper (Cu)	0.01	0.01	0.20	0.16
Iron (Fe)	0.17	0.12	0.42	8.1
Lead (Pb)	0.02	0.13	0.01	0.37
Magnesium (Mg)	7	9	1	4
Manganese (Mn)	0.10	0.48	0.14	2.5
Mercury (Hg)	0.007	<0.5	0.37	<0.05
Molybdenum (Mo)	<1	0.03	<1	0.91
Nickel (Ni)	1.0	0.06	1.5	0.30
Potassium (K)	<1	7.5	16	46
Selenium (Se)	1.0	<0.011	2.4	<0.001
Silicon (Si)	1.7	<1	1.1	<1
Silver (Ag)	0.01	<0.007	0.03	0.05
Sodium (Na)	800	170	2250	1650
Tin (Sn)	<1	<1	<1	<1
Vanadium (V)	<1	0.07	<1	0.67
Zinc (Zn)	0.02	0.04	0.11	0.47
Total carbonate	<1	<1	<1	<1
Chloride (Cl)	620	160	1700	2250
Fluoride (F)	2.4	1.0	0.7	1.5
Sulfite	1.0	41	7.9	1300
Sulfate	2270	1360	4000	3750
Phosphate	<0.1	<0.1	0.41	<0.3
Total nitrogen	<0.005	<0.005	0.002	<0.005
Chemical oxygen demand	105	90	180	190
Total dissolved solids	4100	2100	8700	14000
Total alkalinity	52	130	<1	<1
Conductance, mho/cm	0.0051	0.00293	0.0112	0.014
Turbidity, Jackson units	<1	5	<1	<5
pH	6.54	6.80	1.94	1.38

[a] Concentration in milligrams per liter unless otherwise indicated.

TABLE B-17. ANALYSES OF SCRUBBER LIQUORS FROM DLC PHILLIPS STATION: SINGLE- AND DUAL-STAGE VENTURI SCRUBBER SYSTEMS

(Scrubber test conditions at time of sampling shown in Table B-5)

Scrubber liquor constituents[a]	In-process data		Potential discharge point data		
	Sample location				
	Scrubber effluent		Clarifier underflow		Pond supernate
	Sample date				
	10/4/73	6/17/74	10/4/73	6/17/74	6/17/74
Aluminum (Al)	--	--	--	--	--
Antimony (Sb)	--	--	--	--	--
Arsenic (As)	0.083	0.06	0.09	<0.004	<0.004
Beryllium (Be)	0.012	0.002	0.014	0.002	0.002
Boron (B)	--	--	--	--	--
Cadmium (Cd)	0.022	0.1	0.023	0.01	--
Calcium (Ca)	1300	660	1400	600	613
Chromium (Cr) (total)	0.037	--	0.040	--	--
Cobalt (Co)	--	--	--	--	--
Copper (Cu)	0.06	--	0.07	--	--
Iron (Fe)	--	--	0.026	--	--
Lead (Pb)	0.08	0.5	0.18	0.04	0.4
Magnesium (Mg)	220	--	410	--	--
Manganese (Mn)	--	--	--	--	--
Mercury (Hg)	0.09	0.0004	0.01	0.0002	0.0004
Molybdenum (Mo)	--	--	--	--	--
Nickel (Ni)	--	--	--	--	--
Potassium (K)	20	10	22	26	22
Selenium (Se)	0.8	0.11	0.8	0.028	0.074
Silicon (Si)	--	--	--	--	--
Silver (Ag)	0.02	--	--	--	--
Sodium (Na)	1680	440	2400	340	344
Tin (Sn)	--	--	--	--	--
Vanadium (V)	--	--	--	--	--
Zinc (Zn)	0.12	--	0.09	--	--
Total carbonate	<1	<1	<1	<1	<1
Chloride (Cl)	1800	340	2700	470	420
Fluoride (F)	4.8	8	2.6	10	7
Sulfite	<1	1.7	<1	20	4.8
Sulfate	4500	2700	6450	2730	1000
Phosphate	<0.05	<0.05	<0.05	<0.05	<0.05
Total nitrogen	<0.005	<0.005	<0.005	<0.005	<0.005
Chemical oxygen demand	--	65	--	60	--
Total dissolved solids	9400	4600	14,[illegible]0	4200	4000
Total alkalinity	61	78	--	--	41
Conductance, mho/cm	0.0063	0.0043	0.01	0.0034	0.0030
Turbidity, Jackson units	<1	<1	<1	<1	<1
pH	7.20	8.92	7.11	10.70	10.44

[a] Concentration in milligrams per liter unless otherwise indicated.

TABLE D-18. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM TVA SHAWNEE STEAM PLANT

Date: 1 Feb 1973

Conc: ppm

TCA Scrubber-Limestone System

Scrubber Solids Constituents	Sample Description						
	Coal	Limestone	Fly Ash (In)	Fly Ash (Out)	Bottom Ash	Scrubber Effluent	Clarifier Effluent
Arsenic	4	6	32	50	7	52	33
Beryllium	0.2	6	34	0.2	30	0.2	6
Cadmium	1	0.12	0.42	-	0.4	3	1
Chromium	20	10	230	440	700	15	66
Copper	8	4	25	110	220	9	9
Lead	30	0.1	3	7	1	2	1
Mercury	0.6	-	3	7	0.4	1.2	1
Selenium	3	1	8	2	16	11	2
Zinc	180	-	290	1666	-	-	120

TABLE D-9. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM TVA SHAWNEE STEAM PLANT

Date: 12 Jul 1973

Conc: ppm

TCA Scrubber–Limestone System

Scrubber Solids Constituents	Sample Description					
	Coal	Limestone	Fly Ash (In)	Bottom Ash	Scrubber Effluent	Clarifier Effluent
Arsenic	19	7	12	6	7	-
Beryllium	0.2	3	34	33	0.2	0.3
Cadmium	5	0.6	4	0.4	2.5	3.2
Chromium	10	9	9	17	190	250
Copper	9	2	7	9	20	18
Lead	34	1.5	4	1	27	21
Mercury	0.5	1	3	0.1	0.4	1
Selenium	6	2	7	7	12	5
Zinc	220	-	600	-	-	430

TABLE D-28. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM TVA SHAWNEE STEAM PLANT

Date: 27 Nov 1973

Conc: ppm

TCA Scrubber–Limestone System

Scrubber Solids Constituents	Sample Description						
	Coal	Limestone	Fly Ash (In)	Fly Ash (Out)	Bottom Ash	Scrubber Effluent	Clarifier Effluent
Arsenic	12	1	18	-	-	3	30
Beryllium	0.6	0.5	3	1	3	5	3
Cadmium	1	0.5	2	6	0.3	3	0.7
Chromium	18	8	17	23	13	140	100
Copper	15	4	11	2	17	11	8
Lead	27	2	3	6	4	2	2
Mercury	-	-	-	-	-	-	-
Selenium	4	3	2	-	2	5	7
Zinc	100	200	140	230	130	180	160

TABLE D-21. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM TVA SHAWNEE STEAM PLANT

Date: 15 June 1974

TCA Scrubber-Limestone System

Scrubber Solids Constituents	Sample Description	
	Coal	
Arsenic	16	
Beryllium	0.8	
Cadmium	0.5	
Chromium	12	
Copper	9	
Lead	27	
Mercury	0.07	
Selenium	3	
Zinc	68	

TABLE D-22. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM SCE MOHAVE GENERATING STATION

Date: 30 Mar 1973

Conc: ppm

TCA Scrubber-Limestone System

Scrubber Solids Constituents	Sample Description				
	Coal	Fly* Ash	Scrubber Effluent	Centrifuge Effluent (Centrate)	
Arsenic	3	9	0.8	0.6	
Beryllium	<0.1	2	0.06	0.05	
Cadmium	0.6	<0.5	0.5	0.5	
Chromium	45	105	9	10	
Copper	50	50	8	9	
Lead	4	25	0.25	0.23	
Mercury	0.05	0.05	0.005	0.001	
Selenium	1.5	10	5	8	
Zinc	10	50	40	45	

*Data from Reference

TABLE D-23. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM TVA SHAWNEE STEAM PLANT

Date: 19 Mar 1974

Conc: ppm

Venturi-Spray Tower-Lime Process

Scrubber Solids Constituents	Sample Description					
	Coal	Fly Ash (In)	Bottom Ash	Scrubber Effluent	Clarifier Effluent	Filter Cake
Arsenic	10	75	5	13	18	13
Beryllium	2	12	3	8	8	11
Cadmium	10	40	1	20	15	4
Chromium	7	50	6	25	20	15
Copper	12	80	16	35	28	30
Lead	40	60	5	25	25	15
Mercury	0.5	0.4	0.6	0.2	0.1	0.2
Selenium	3.4	4	0.7	6.5	7.2	7.8
Zinc	280	350	90	130	280	200

TABLE D-24. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM APS CHOLLA POWER PLANT

Date: 1 April 1974

Conc: ppm

Venturi-Absorption Tower-Limestone System

Scrubber Solids Constituents	Sample Description				
	Coal	Limestone	Fly Ash	Slurry Tank Effluent	Absorption Tower Effluent
Arsenic	2.1	<0.1	0.4	2	0.8
Beryllium	0.5	–	2	1	0.2
Cadmium	0.1	0.02	0.03	0.08	0.06
Chromium	12	11	166	52	48
Copper	39	2	31	76	6
Lead	60	0.5	165	80	14
Mercury	0.05	–	–	4	5
Selenium	5	2	5	17	2
Zinc	35	–	158	126	60

TABLE D-25. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM DLC PHILLIPS STATION

Date: 4 Oct 1973

Conc: ppm

Venturi-Lime System

Scrubber Solids Constituents	Sample Description	
	Coal	Lime
Arsenic	16	<2
Beryllium	0.4	0.02
Cadmium	4	0.03
Chromium	60	6
Copper	30	3
Lead	45	0.1
Mercury	-	-
Selenium	8	22
Zinc	80	300

TABLE D-26. TRACE METAL ANALYSIS OF SCRUBBER SOLIDS FROM DLC PHILLIPS STATION

Date: 17 June 1974

conc: ppm

Venturi-Lime System

Scrubber Solids Constituents	Sample Description	
	Coal	
Arsenic	6	
Beryllium	0.8	
Cadmium	0.5	
Chromium	12	
Copper	11	
Lead	12	
Mercury	-	
Selenium	3	
Zinc	30	

TABLE D-27. TRACE METAL ANALYSES OF SCRUBBER SOLIDS FROM GE INDUSTRIAL BOILER

Date: 18 Jul 1974

Conc: ppm

Bubble Cap Scrubber-Double Alkali System

Scrubber Solids Constituents	Sample Description	
	Coal	
Arsenic	14	
Beryllium	1	
Cadmium	0.4	
Chromium	7	
Copper	18	
Lead	16	
Mercury	0.4	
Selenium	6	
Zinc	27	

APPENDIX E

EFFECT OF SCRUBBING PROCESS VARIABLES ON WASTE SYSTEM CHEMISTRY DATA PLOTS

The following figures show the trace element relationships (or lack of relationships) that were observed within the liquor portion of scrubber samples as a function of in-process changes. In each case, major chemical changes during the wet-end processing of scrubber wastes have been identified. The following figures show those changes in trace element content as a consequence of changes in the major chemical species. Relationships were not observed in every case, and the lack of a function relationship with a major chemical change is presented since the result may be important for the proper interpretation of overall results.

Discussions of these data are presented in Section 7.4 and relate to functional relationships between trace metal content in scrubber liquor and process variables.

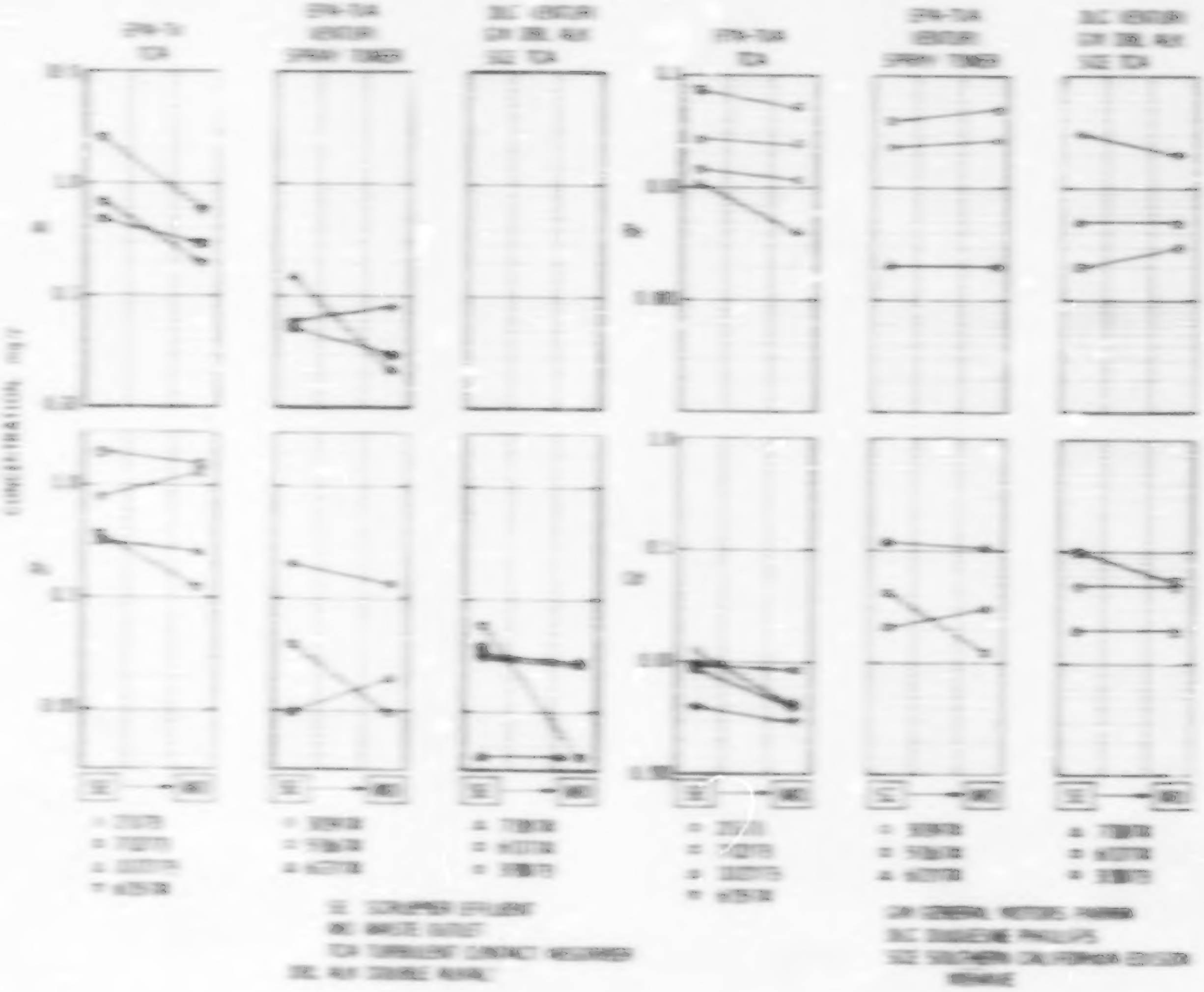


Figure E-1. Changes in chemical concentration of system liquor as it proceeds from scrubber effluent to waste outlet.

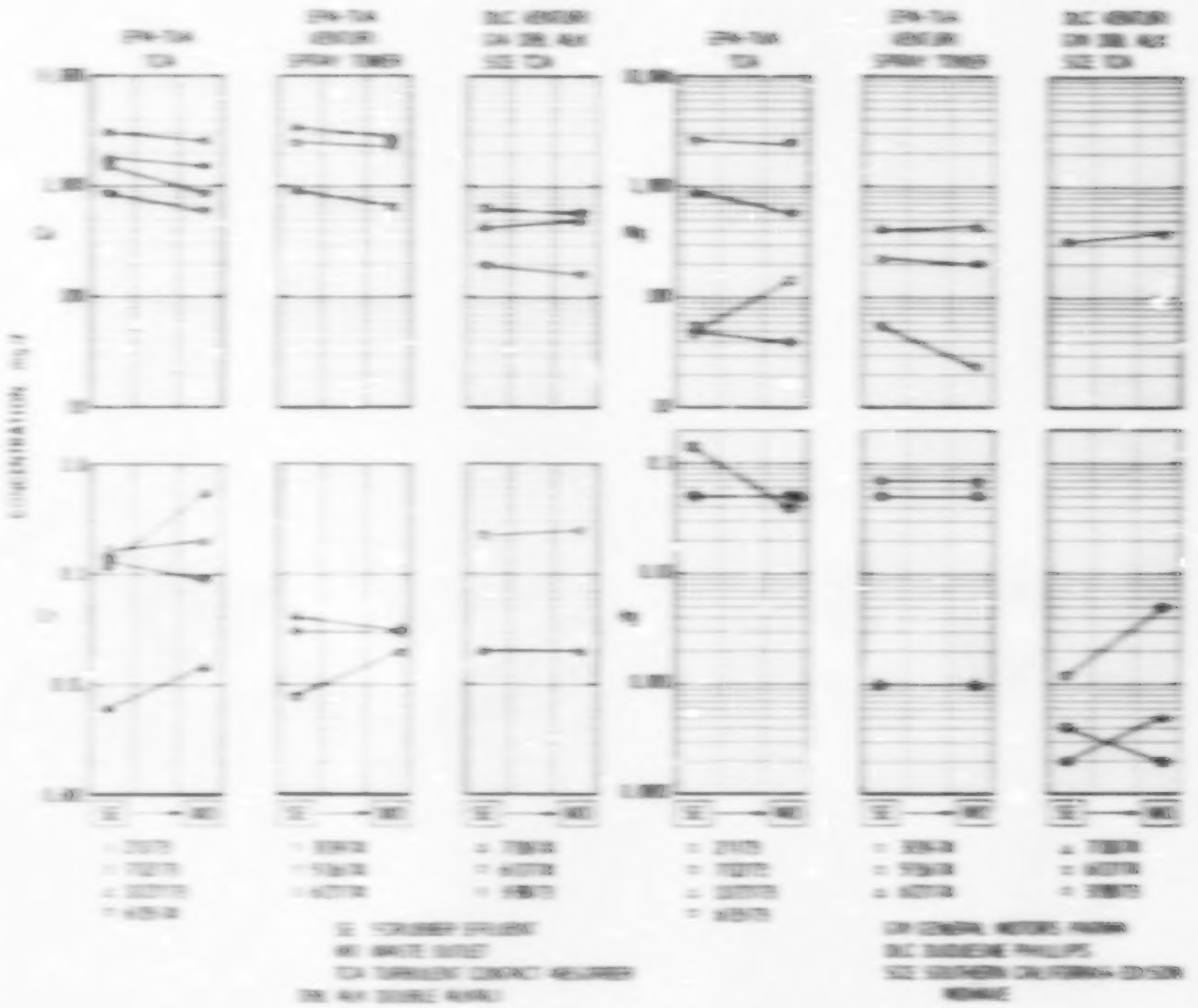


Figure E-1. Continued

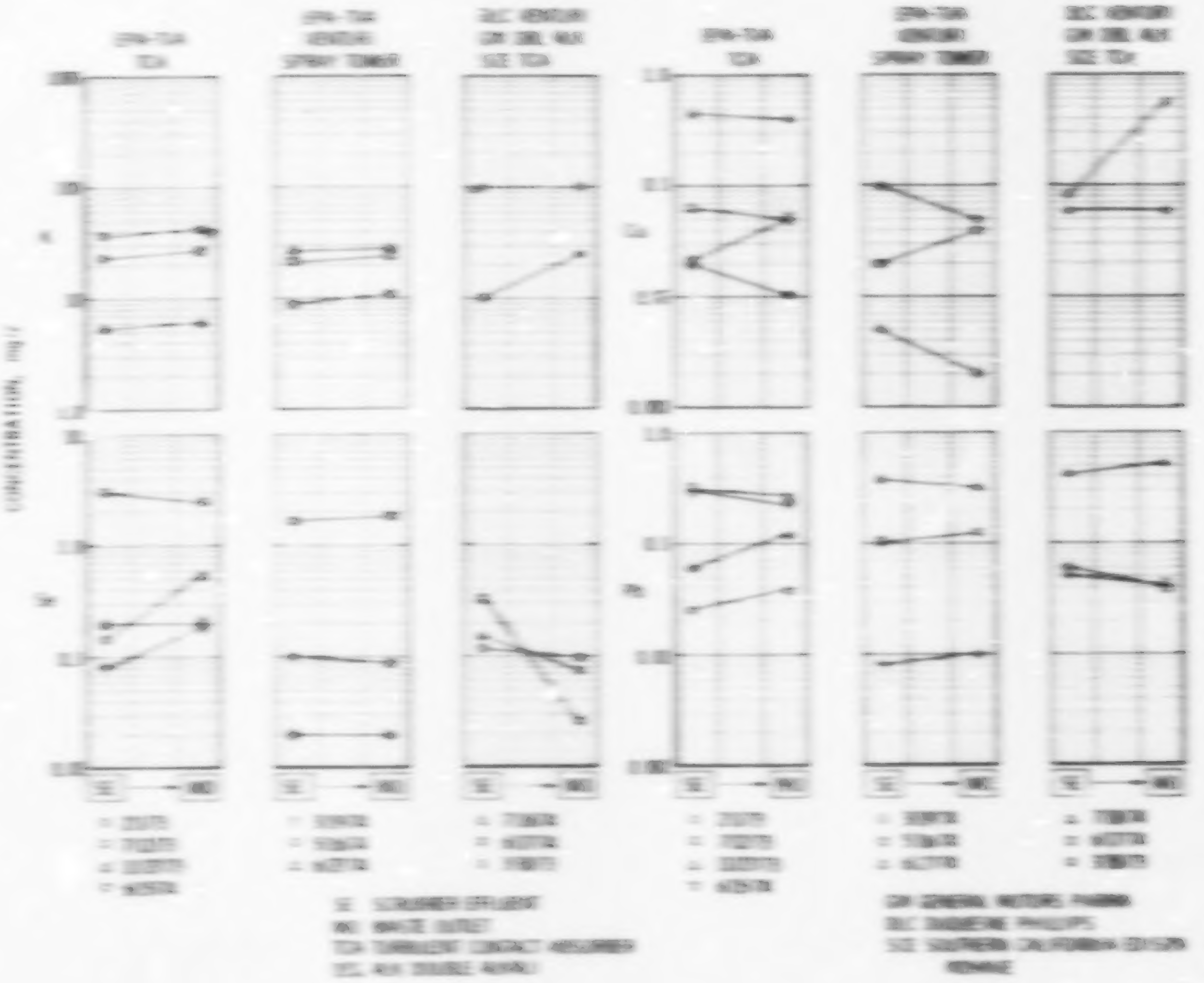


Figure E-1. Continued

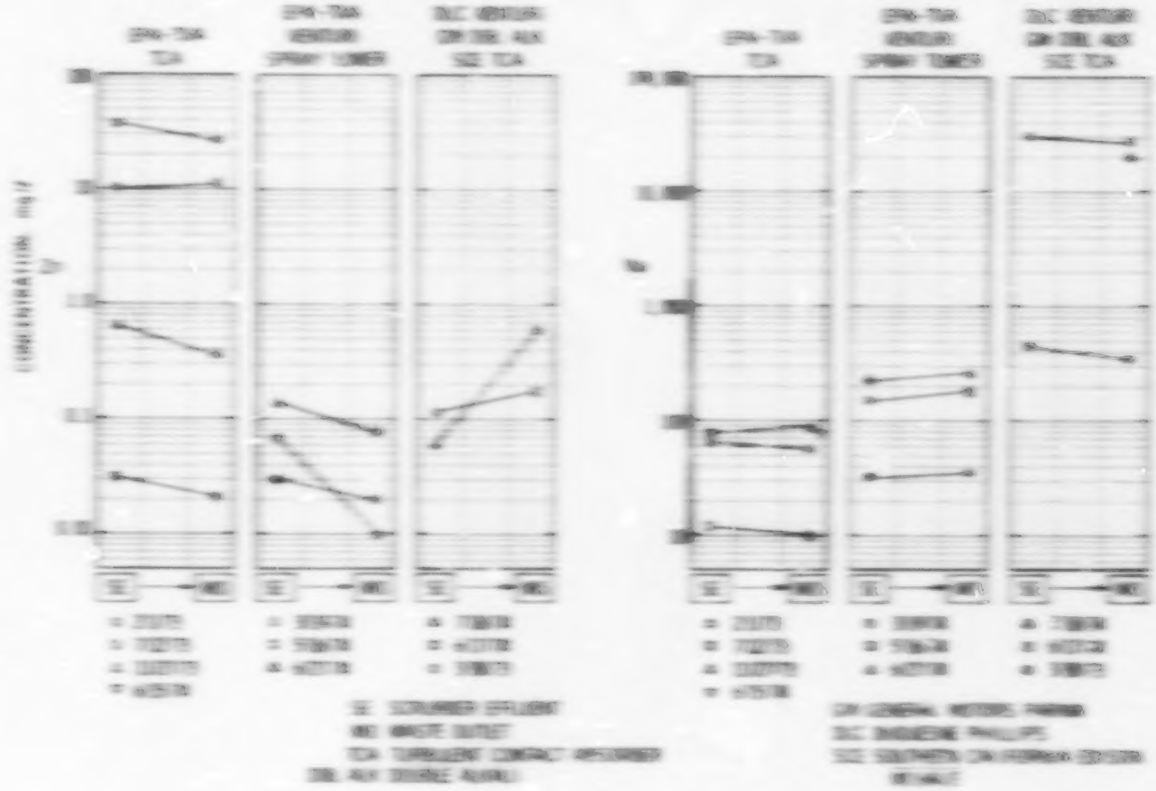


Figure E-1. Continued

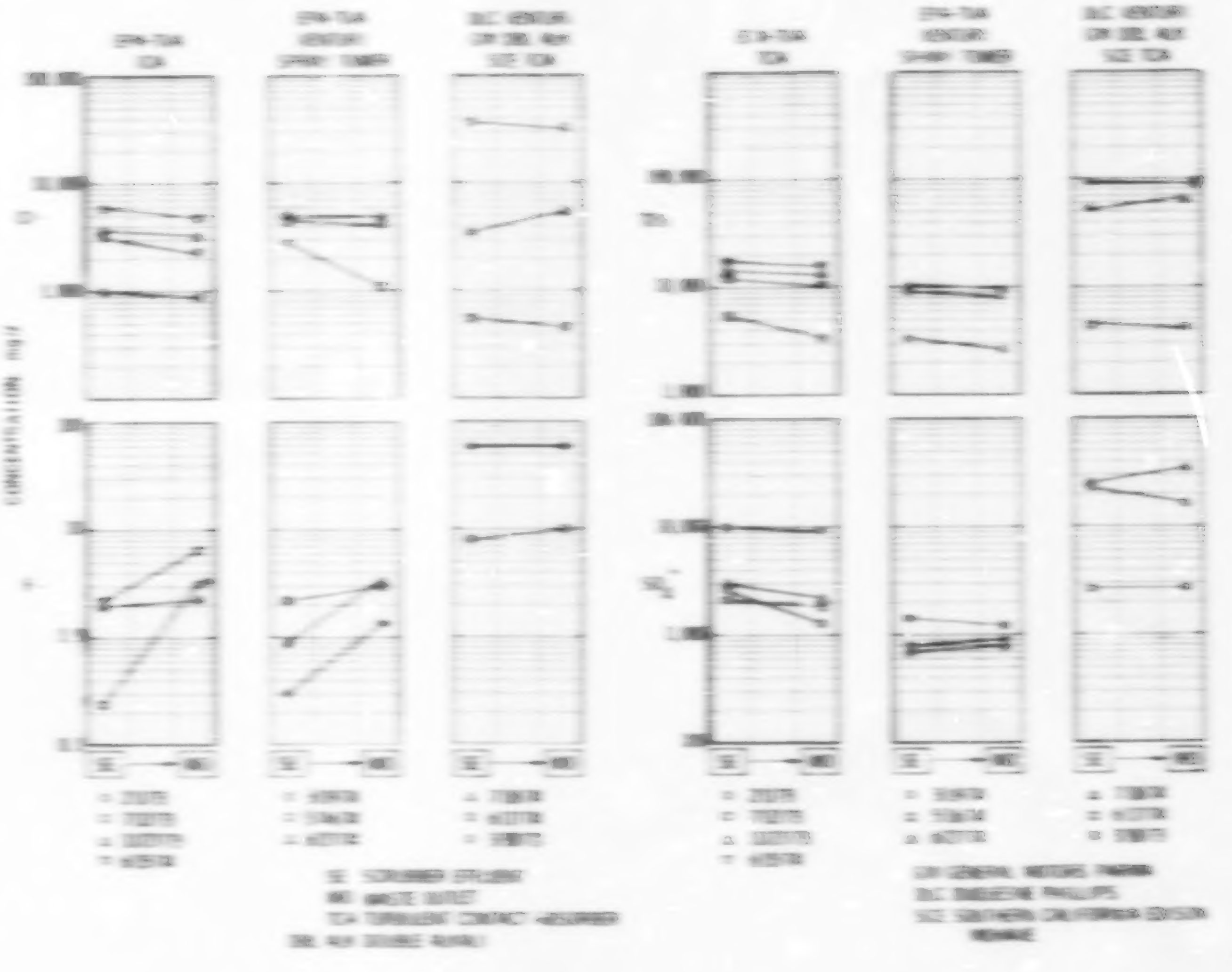


Figure E-1. Continued

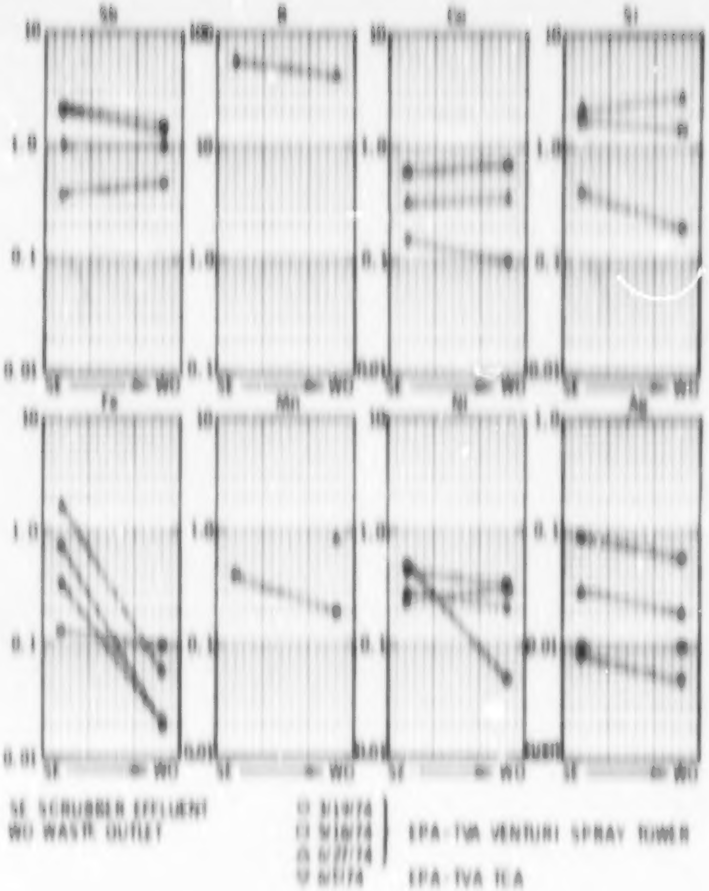


Figure E-1. Continued

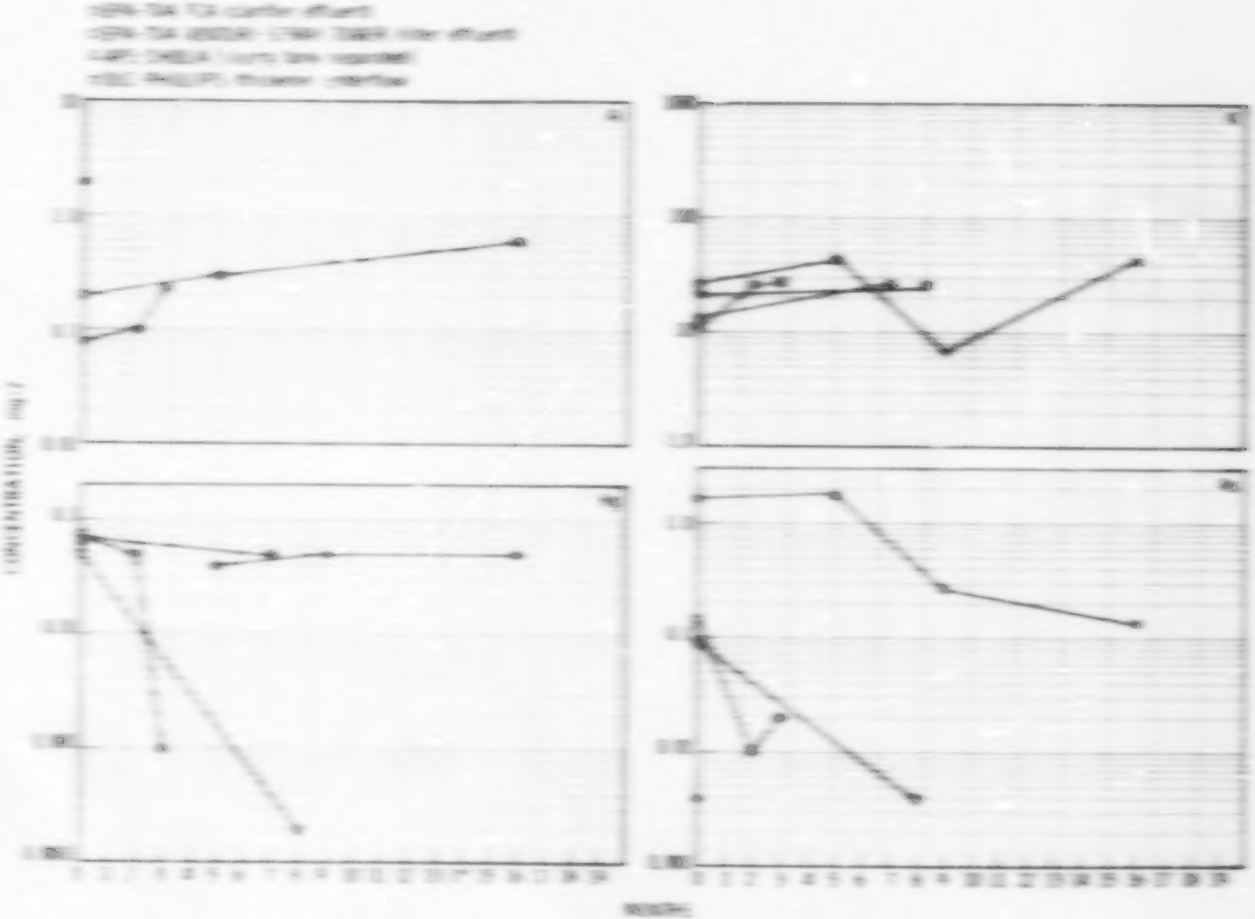


Figure E-2. Change in chemical concentration of system liquor as a function of time of scrubber operations.

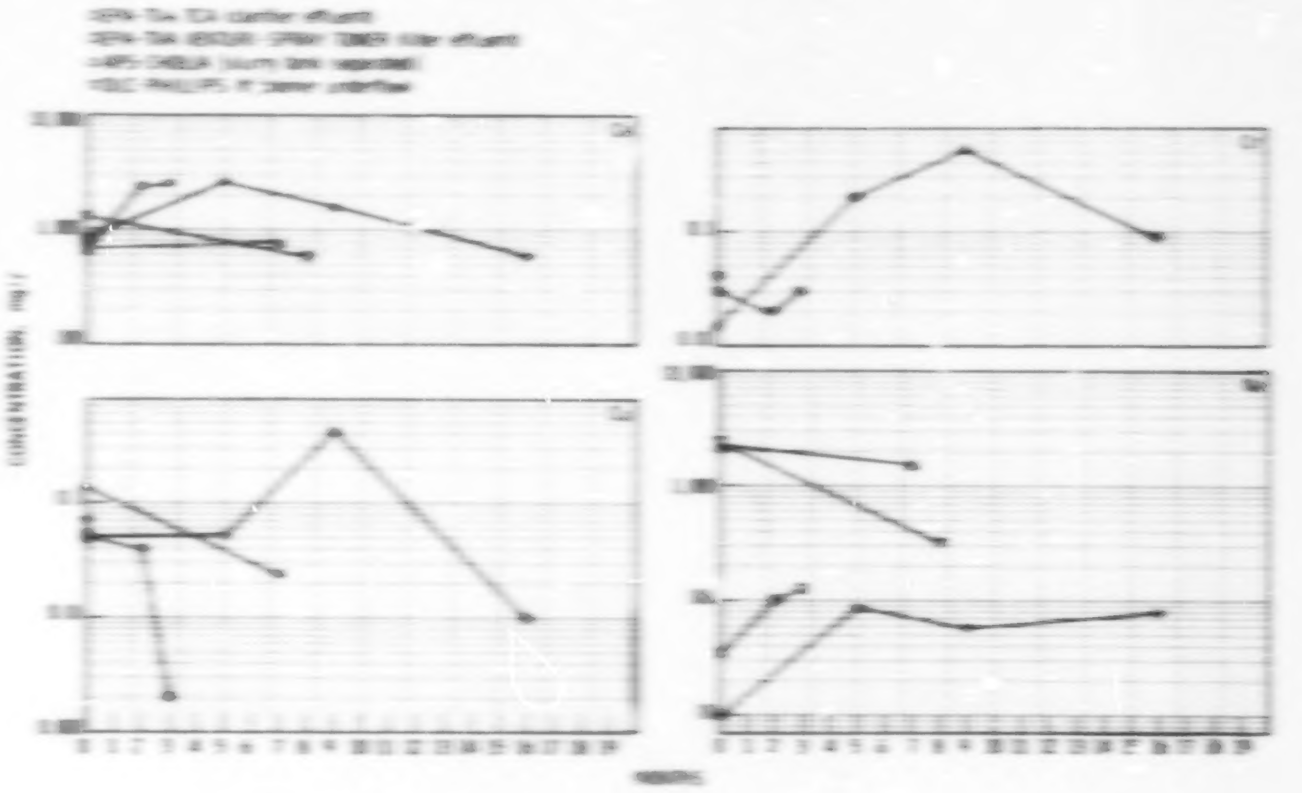
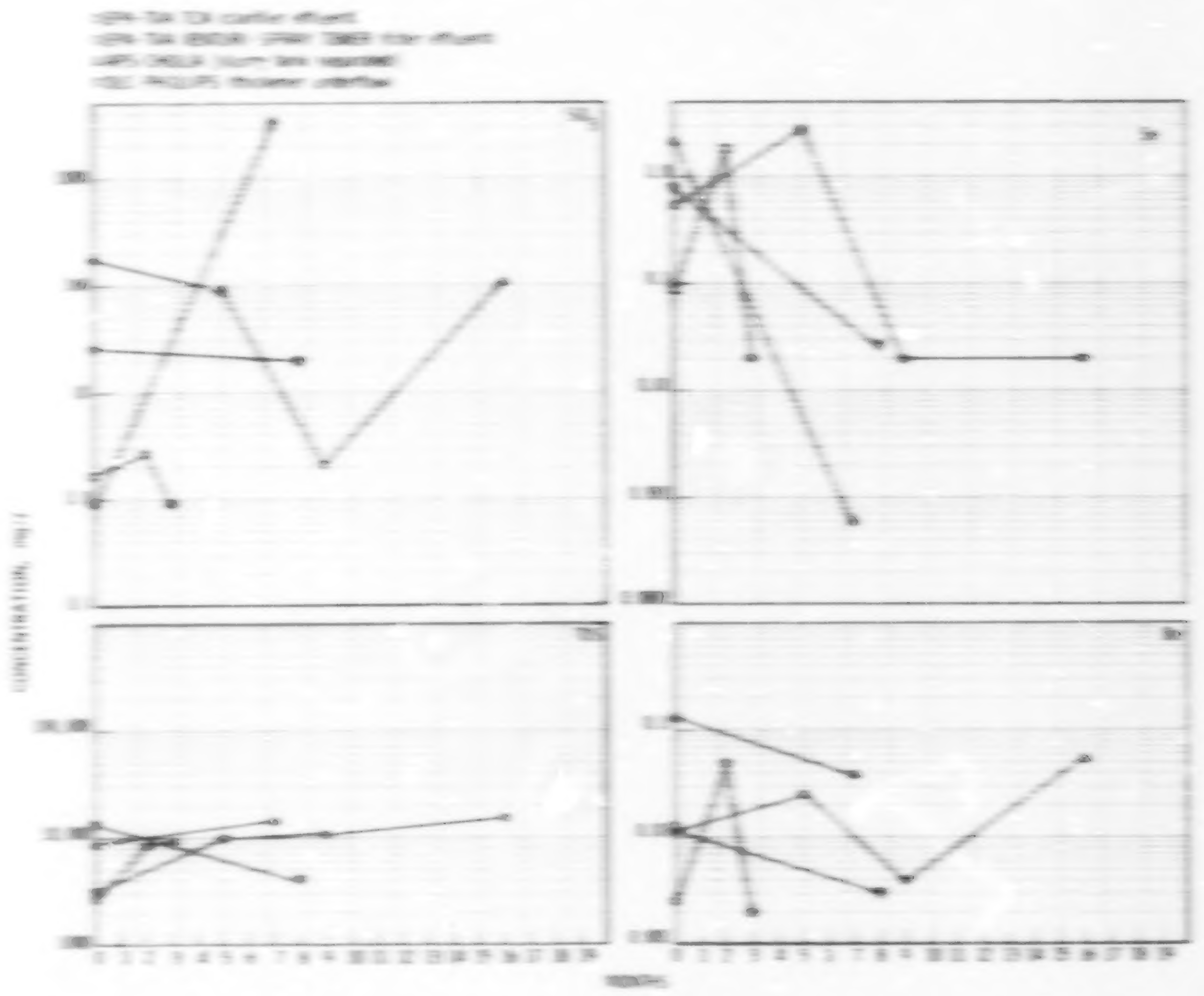


Figure E-2. Continued



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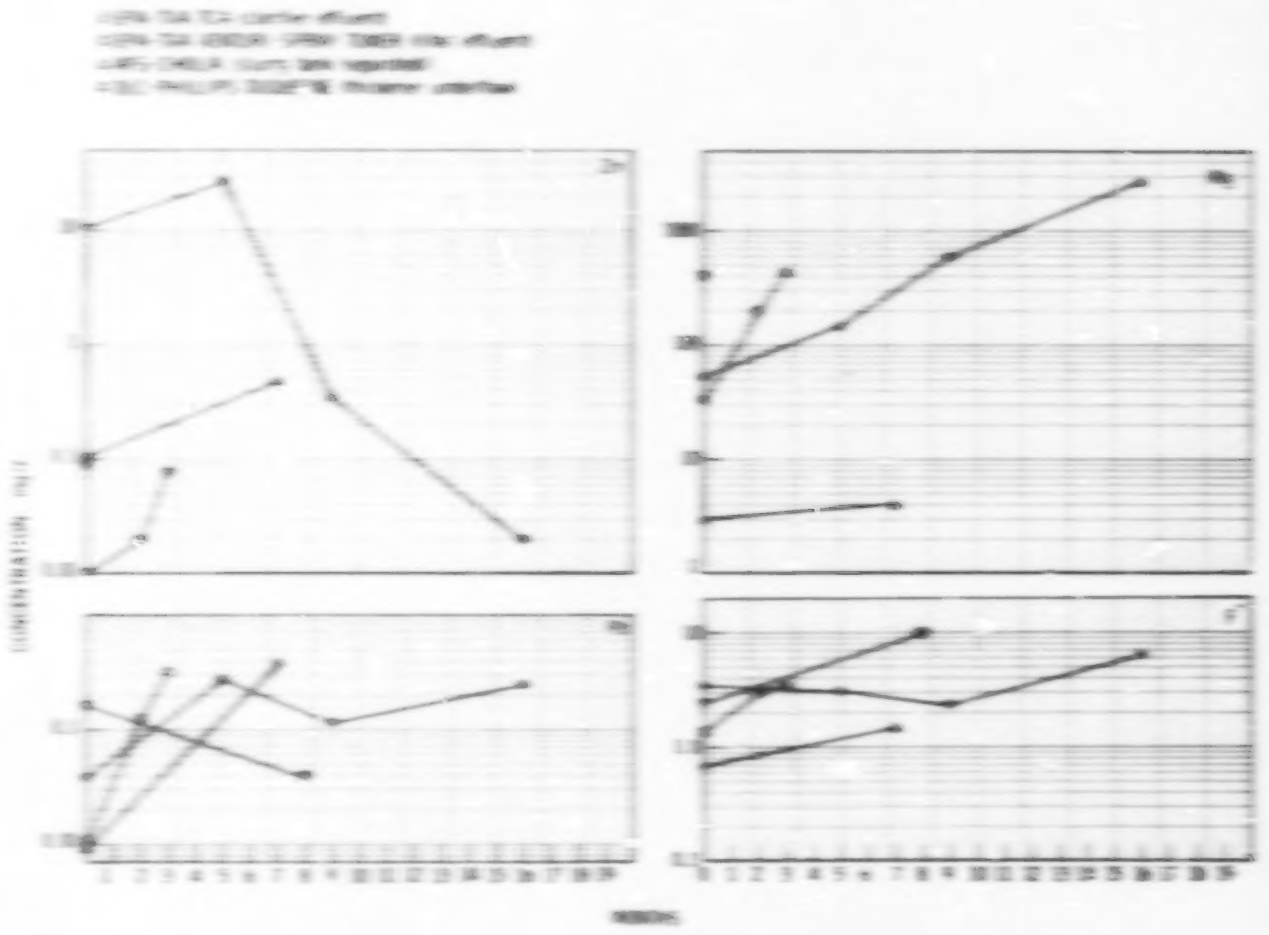

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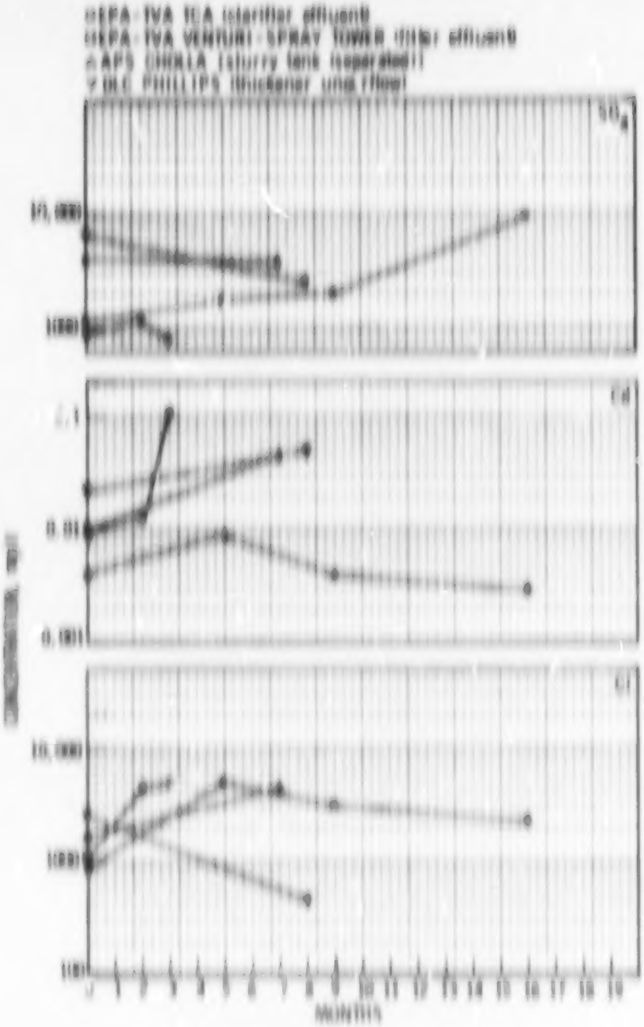

Figure E-2. Continued

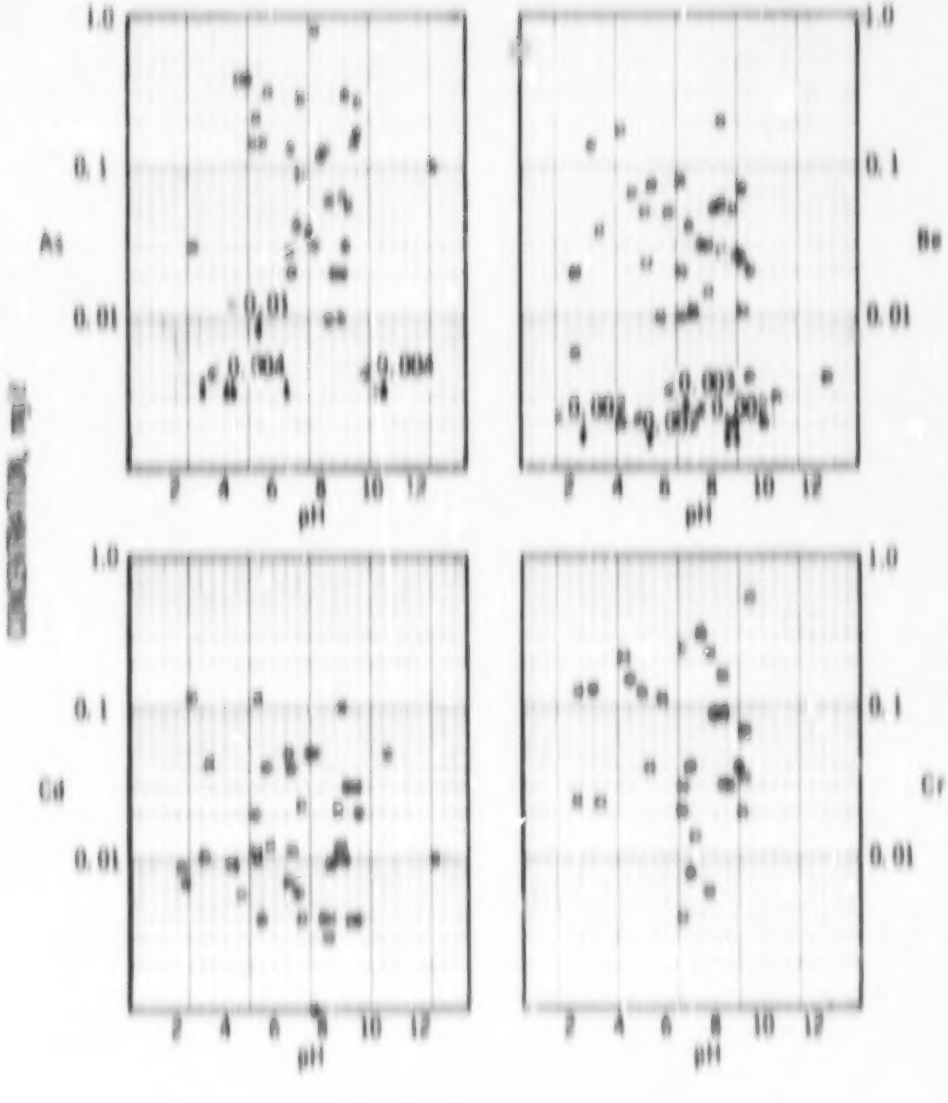

Figure E-1. Trace element concentration in system liquor as a function of system pH.

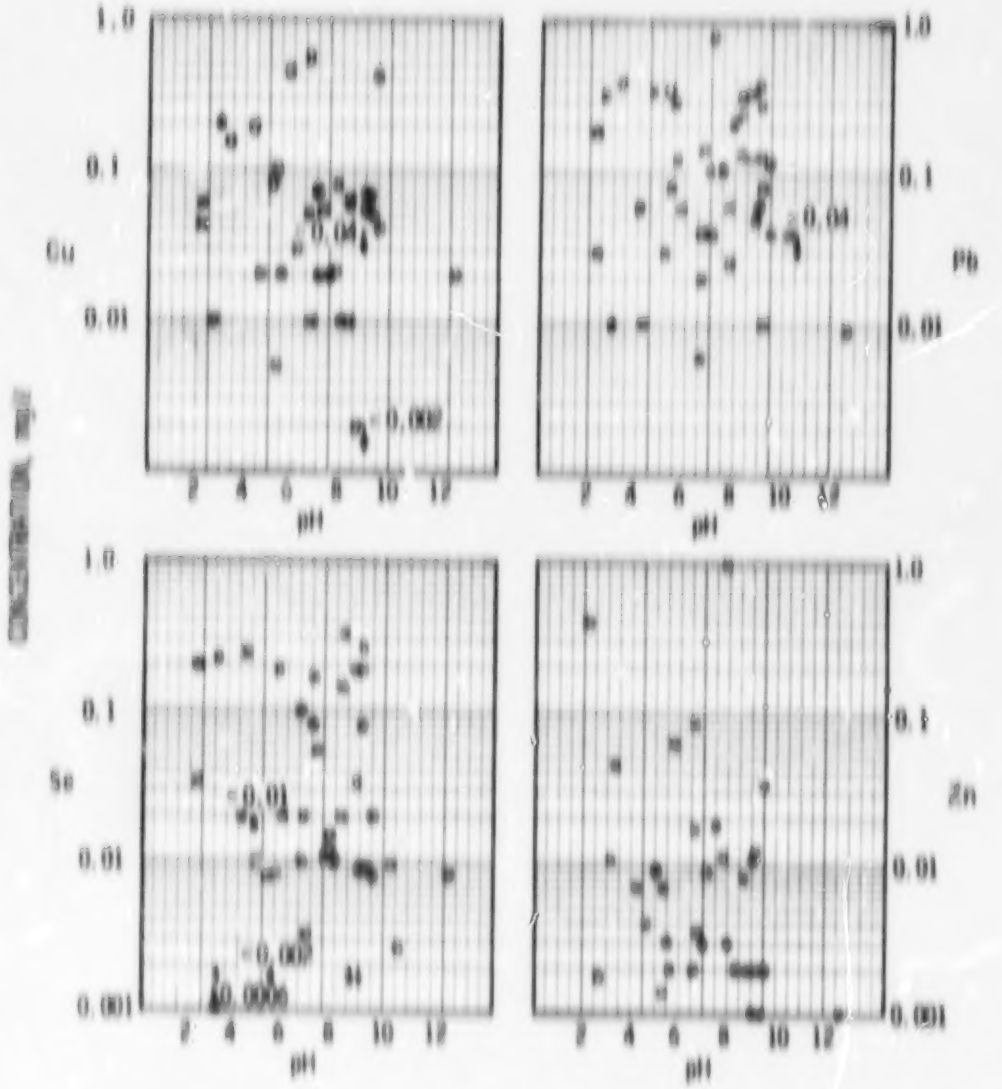

Figure E-3. Continued

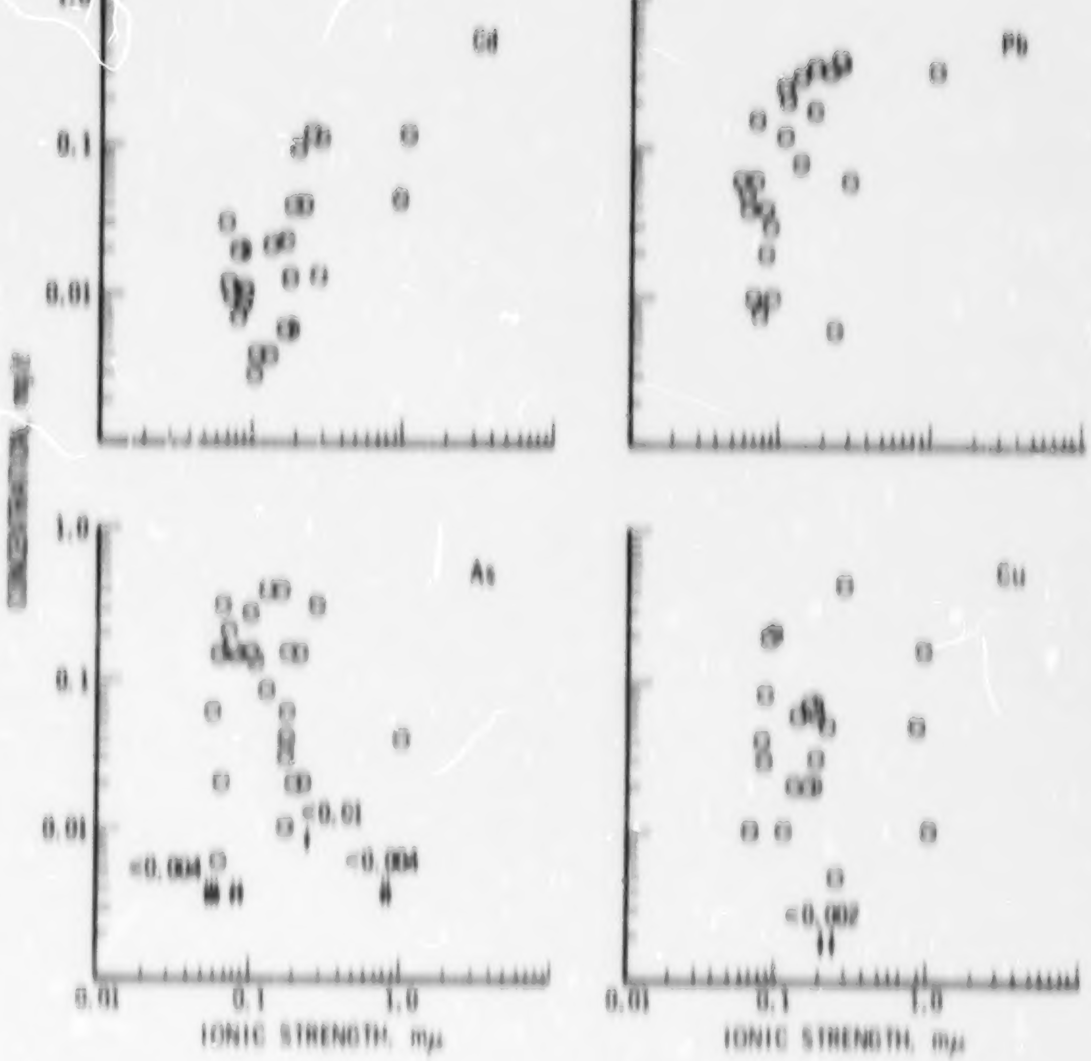

Figure E-4. Trace element concentration of system liquor as a function of system ionic strength.

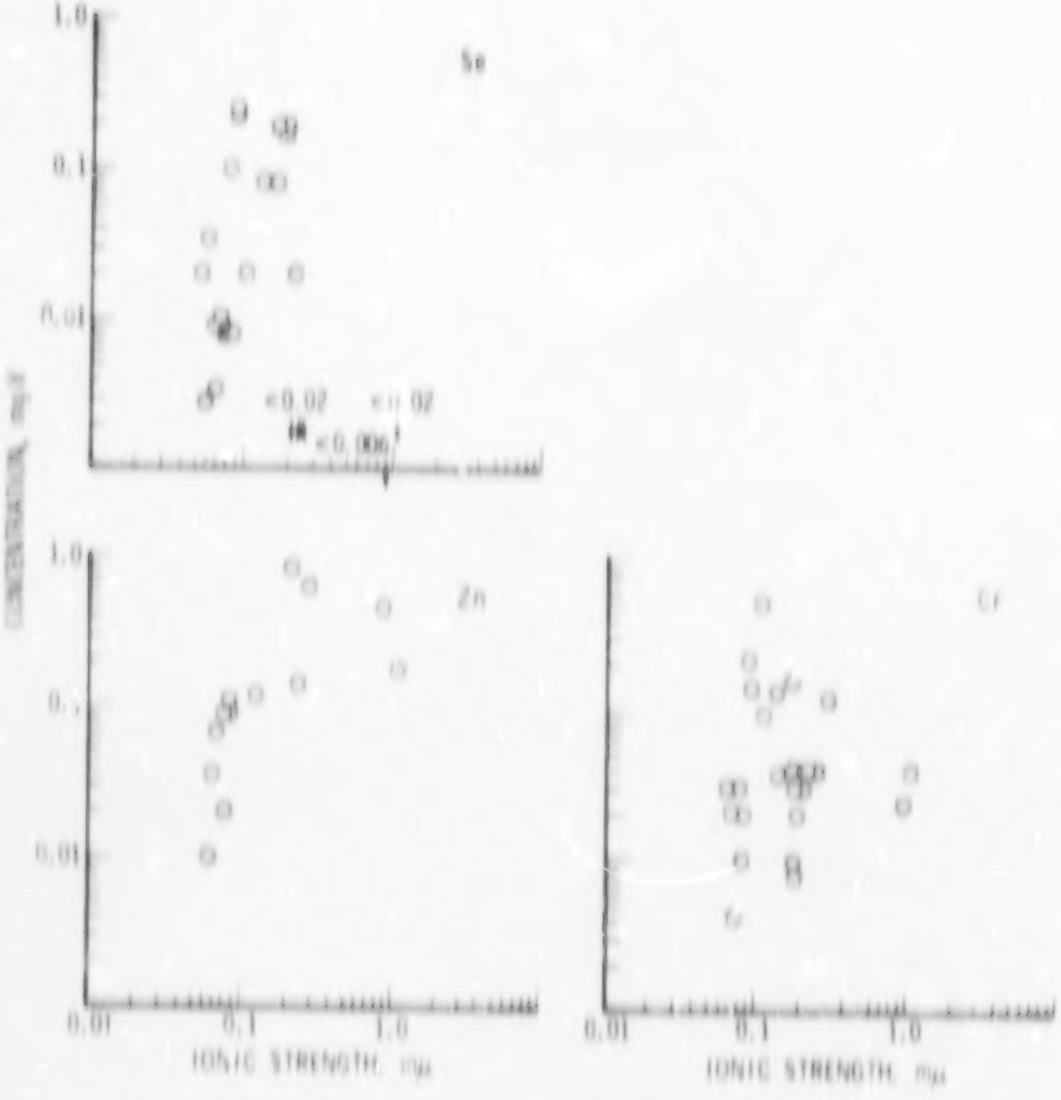

Figure E-4. Continued

APPENDIX F

MATHEMATICAL DETERMINATION OF PROGRAM SCRUB

A solid of composition $M_m N_n$ upon dissolution dissociates into m positive ions M^{z+} and n negative ions N^{z-} per mole, where z is the ionic charge. The thermodynamic equilibrium constant K for the dissolution process is given by

$$K = a_M^m \, a_N^n = c_M^m \, \gamma_M^m \, c_N^n \, \gamma_N^n \tag{F-1}$$

where a represents activities, c is the molar concentration, and γ is the activity coefficient of the respective ions. (The activity of the solid phase is unity by definition.) Since activity coefficients of individual ions are undefined theoretically and impossible to determine experimentally, the mean activity coefficient of the electrolyte $\gamma_\pm$ is used:

$$\gamma_\pm = \left(\gamma_M^m \, \gamma_N^n\right)^{1/(m+n)} \tag{F-2}$$

Therefore,

$$K = c_M^m \, c_N^n \, \gamma_\pm^{m+n} \tag{F-3}$$

The solubility product constant K_{sp}, which is defined as a product of molar concentrations

$$K_{sp} = c_M^m \, c_N^n = K \gamma_\pm^{-(m+n)} \tag{F-4}$$

is dependent on the ionic strength of the solution μ and becomes equal to the thermodynamic equilibrium constant $K = K_{sp}(\mu \to 0)$, or $K = K_{sp}^0$ as μ approaches zero and, therefore, as $\gamma_\pm$ approaches unity. The ionic strength is defined as

$$\mu = 0.5 \, \Sigma c_i \, z_i^2 \tag{F-5}$$

From the modified form of the Debye-Huckel expression,

$$-\log \gamma_\pm = \frac{A_\pm | z^+ z^- | \mu^{1/2}}{1 + B\mu^{1/2}} - C\mu \tag{F-6}$$

where A, B, and C are empirical constants, and the mean activity coefficient can be related to the ionic strength. The alternative power series form of the Debye-Huckel equation leads to following empirical expression if only the first two terms are retained:

$$-\log \gamma_\pm \cong A'\mu^{1/2} - C'\mu \tag{F-7}$$

Taking the logarithm of the equation relating K_{sp} and K

$$\log K_{sp} = \log K^0_{sp} - (m + n) \log \gamma_\pm \tag{F-8}$$

and substituting for $\log \gamma_\pm$, one has the final relationship which is used in Program SCRUB:

$$\log K_{sp} = \log K^0_{sp} + X\mu^{1/2} - Y\mu \tag{F-9}$$

or one may use the relation

$$pK_{sp} = -\log K_{sp} \tag{F-10}$$

and

$$pK_{sp} = pK^0_{sp} - X\mu^{1/2} + Y\mu \tag{F-11}$$

where X and Y are empirical constants obtained from experimental data reported in the literature (38, 39). If X and Y and $K^0_{sp} = K$ are known for each slightly soluble component of the liquor, then it is only necessary to determine the ionic strength in order to obtain the molar concentration and, therefore, the solubility of each component. Usually, an iterative procedure will be necessary to calculate μ, but convergence is rapid so that fewer than five iterations will suffice to obtain 10 percent accuracy.

Experimental data were found in the literature (38, 39) from which the values of pK^0_{sp}, X, and Y were determined:[†]

	pK^0_{sp}	X	Y
$CaSO_4$	4.63	2.77	1.06
$CaSO_3$	6.50	2.76	1.06
$CaCO_3$	8.27	2.21	0.87
$Ca(OH)_2$	5.04	1.59	0.81

It is evident that, for the four calcium compounds listed, there was only a slight variation in the values of X and Y. Similar results were observed for compounds of lead and mercury:

	pK^0_{sp}	X	Y
$PbSO_4$	7.79	2.87	1.28
$PbCO_3$	13.13	3.22	1.12
Hg_2SO_4	6.17	3.21	1.28

Although data were found to provide the required constants for all the weak acids involved (exceptions being H_2SeO_3 and H_3AsO_4), no additional determinations of pK_{sp} over a sufficiently wide range of ionic strength were found in the literature.[†] In view of the similarity of X and Y values for the calcium, lead, and mercury compounds, it was decided to use the values for $CaSO_4$ for all insoluble sulfates; the values of X and Y for $CaSO_3$ were used for all insoluble sulfites and, similarly, for the carbonates and hydroxides.

With the use of the empirical constants, X and Y for calcium sulfate, the concentration ratios calculated with computer program SCRUB from the calcium and sulfate concentrations obtained from analyses of sludge liquors differed systematically from unity. The mean ratio was approximately 1.2.

[†] It should be noted that the pK_{sp} data reported in the literature from which the values of X and Y have been calculated were obtained by adjusting the ionic strength of the solutions with $NaClO_4$. This medium has a different influence on the activity coefficients of ions than the sludge liquors which are of interest here.

Since analytical data were available for a large number of sludge liquor samples which were evidently saturated with gypsum, it was possible to obtain revised values of X and Y for calcium sulfate from these data. Least squares fitting of the data for 153 sludge liquor samples was used to obtain revised values of 4.13 for X and 2.09 for Y. From these revised constants the mean concentration ratio obtained with computer program SCRUB for the 153 samples was 1.00 with a standard deviation of 0.30. It is apparent that these revised constants give better agreement between calculated and experimental data for sludge liquors saturated with gypsum. Therefore, they have been incorporated in program SCRUB and were used to generate the calculated results included in this report.

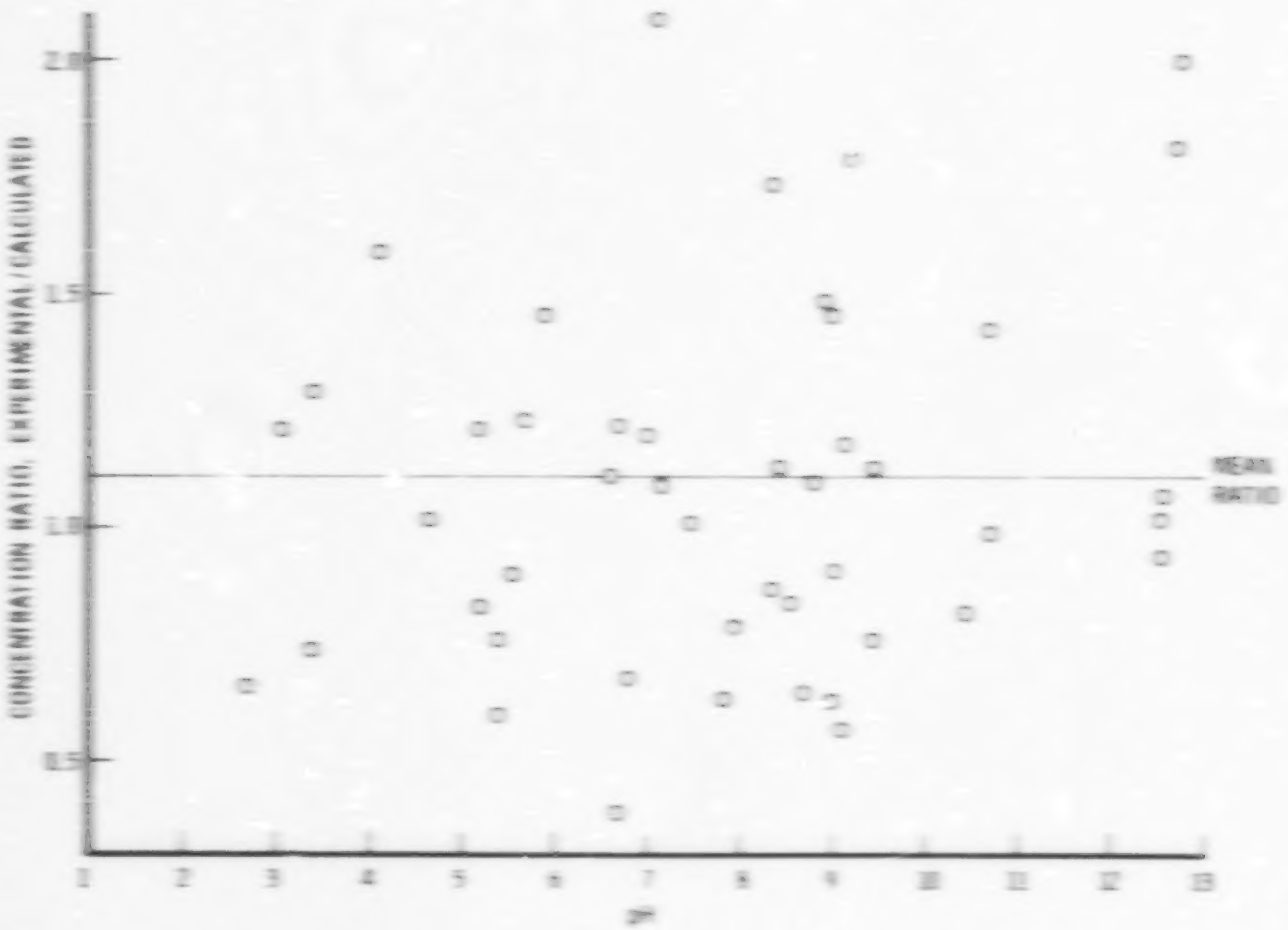

Figure F-1. Concentration ratio as a function of pH.

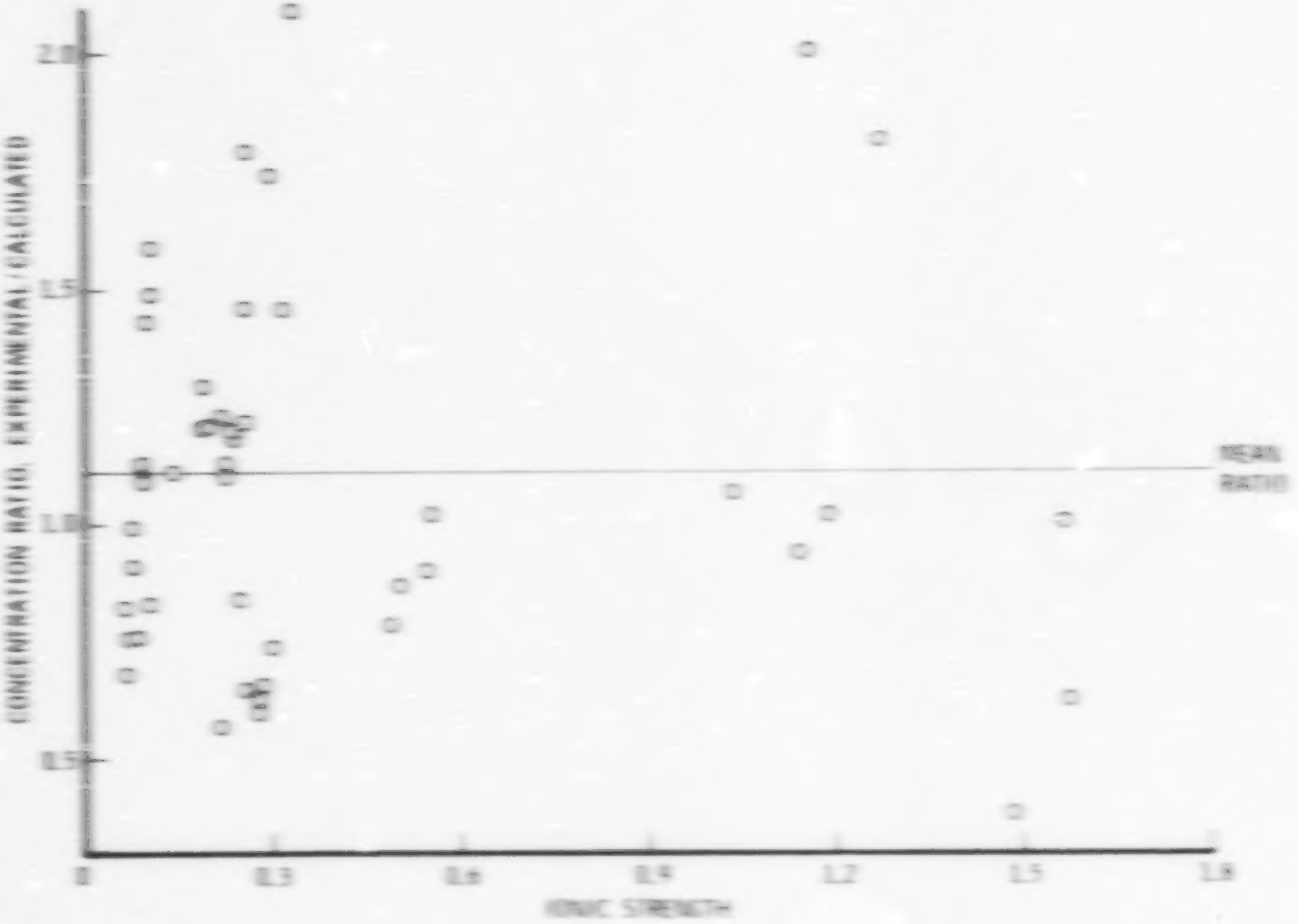

Figure F-2. Concentration ratio as a function of ionic strength.

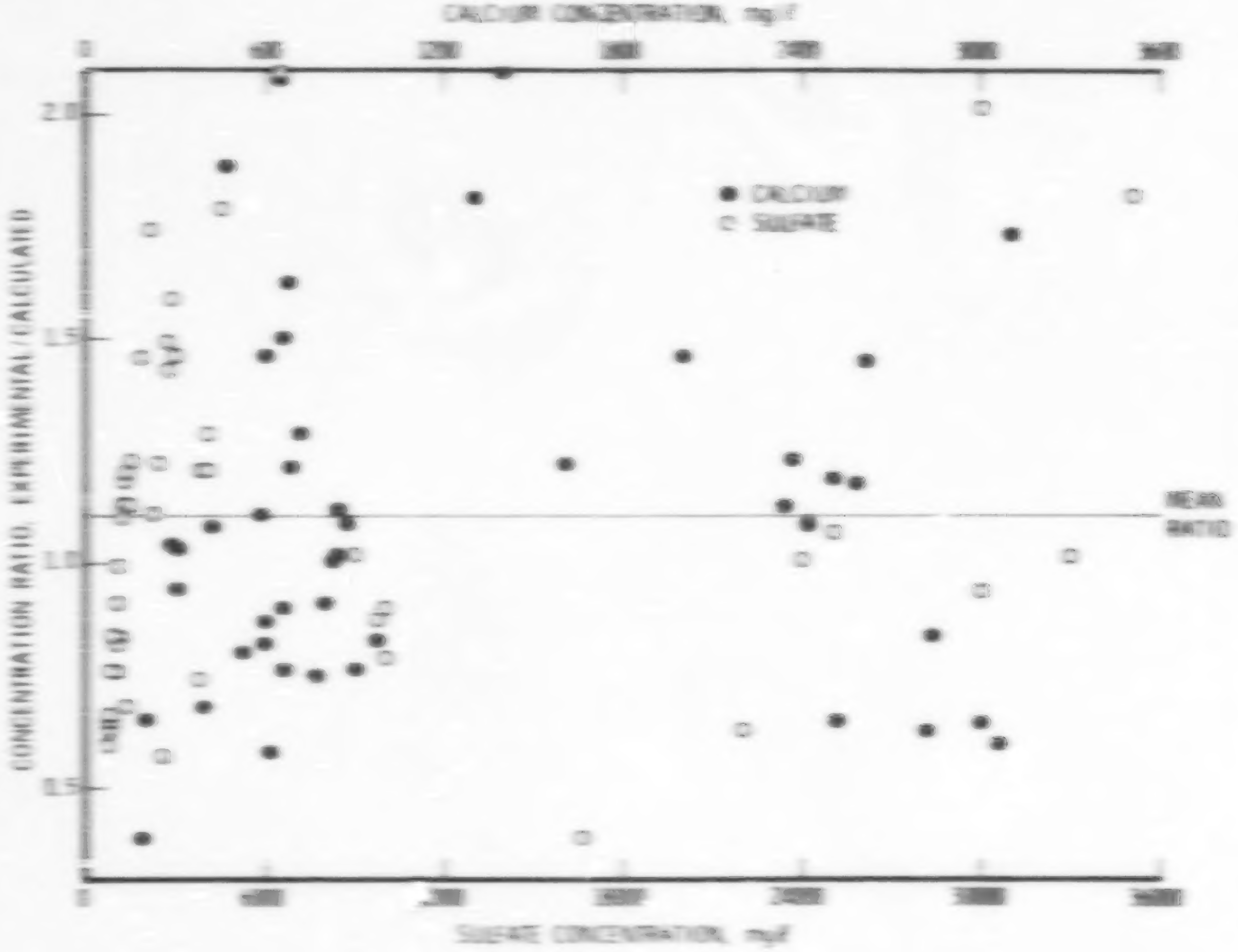

Figure F-1. Concentration ratio as functions of calcium and sulfate concentrations.

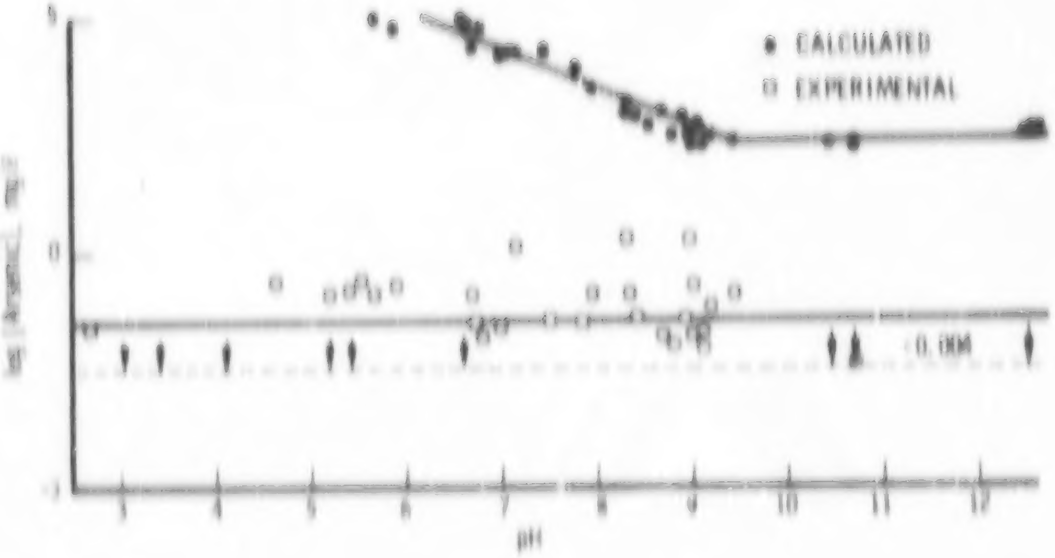

Figure F-4. Comparison of experimental and calculated concentrations of arsenic.

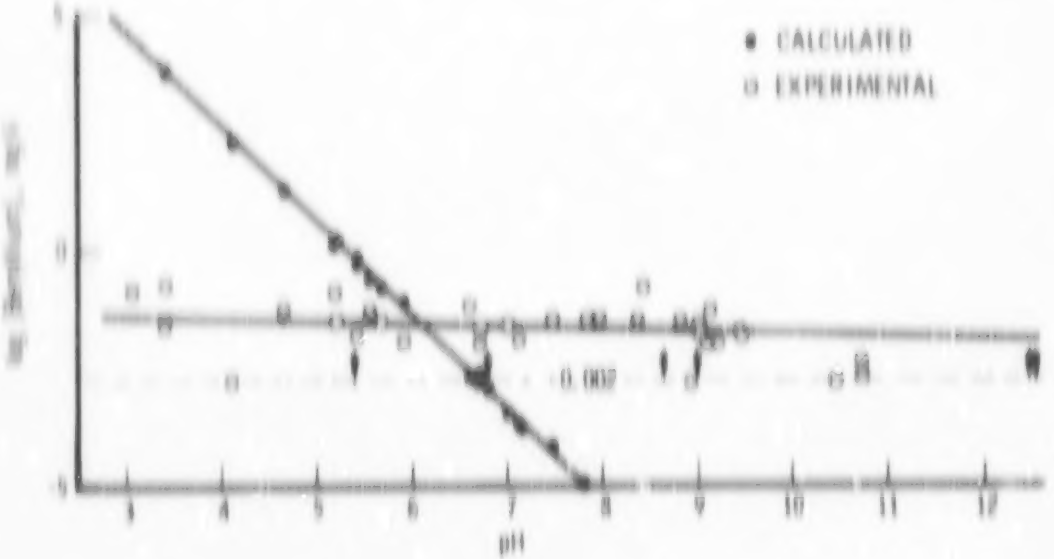

Figure F-5. Comparison of experimental and calculated concentrations of beryllium.

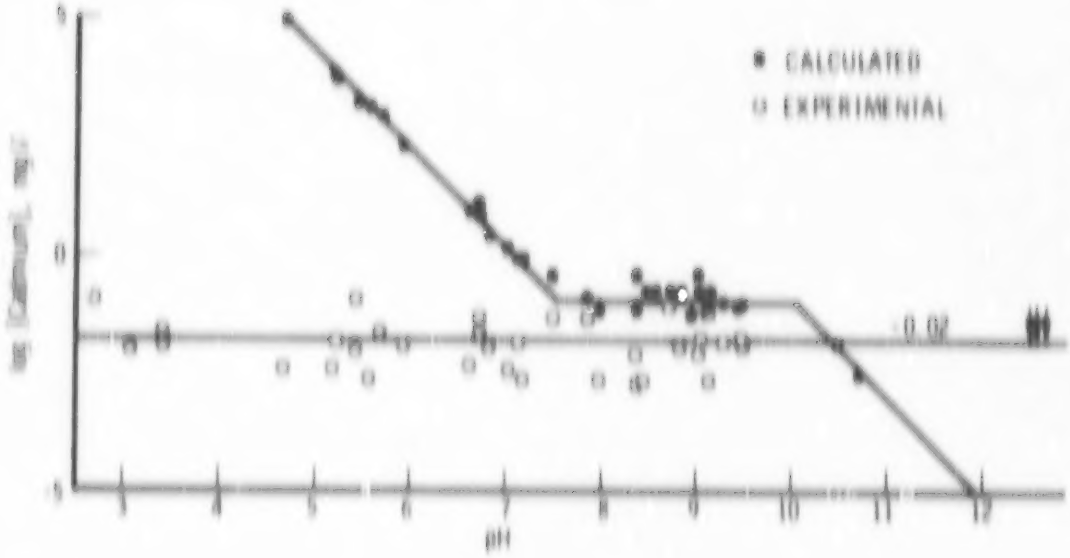

Figure F-6. Comparison of experimental and calculated concentrations of cadmium.

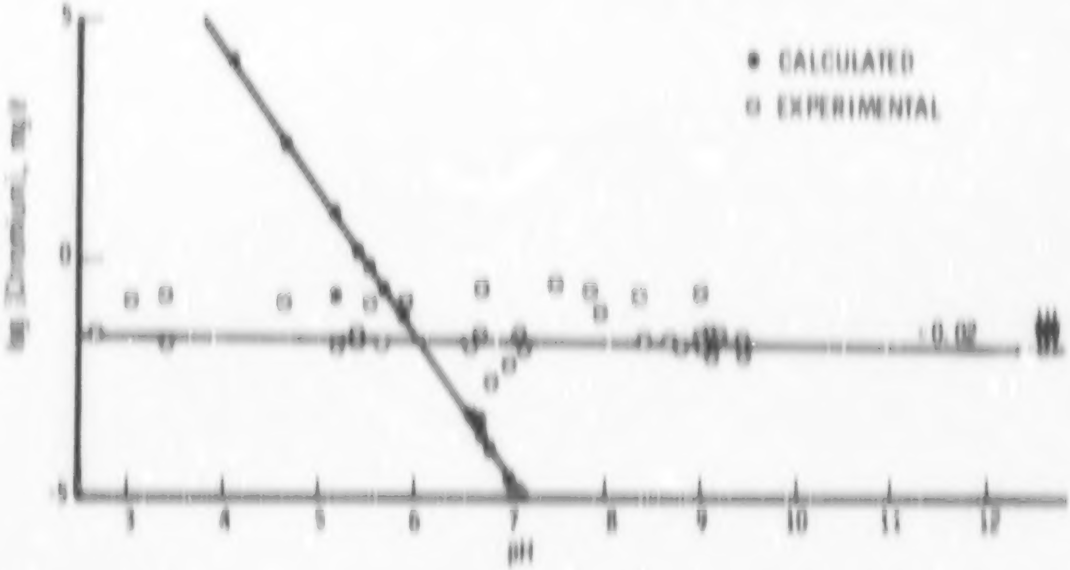

Figure F-7. Comparison of experimental and calculated concentrations of chromium.

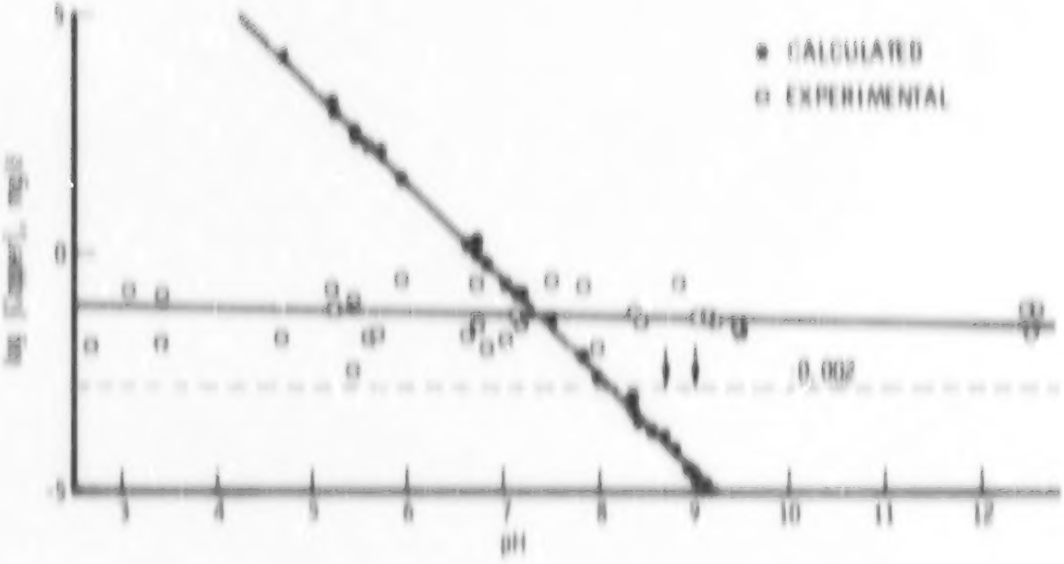

Figure F-8. Comparison of experimental and calculated concentrations of copper.

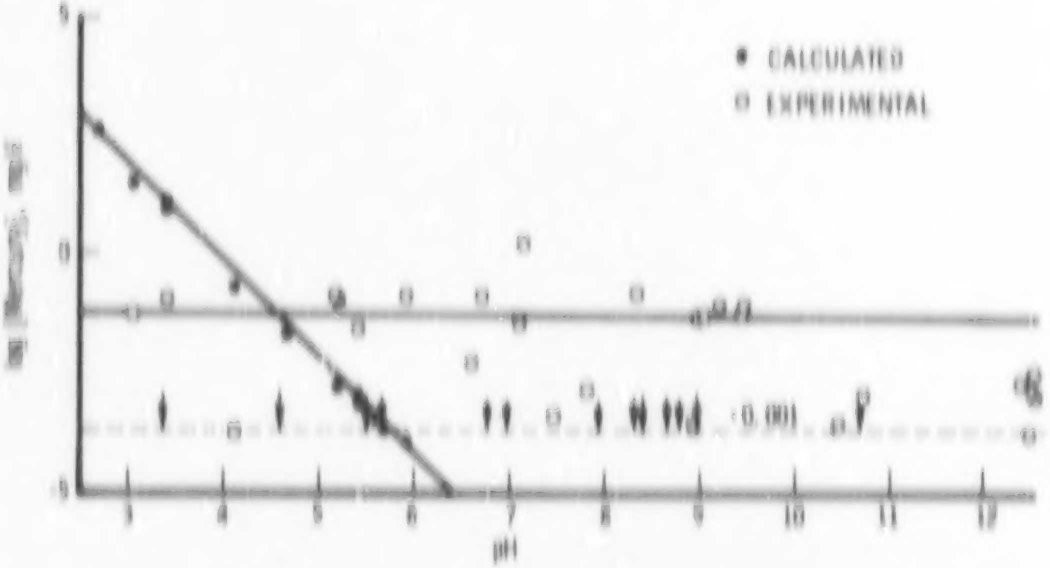

Figure F-9. Comparison of experimental and calculated concentrations of mercury.

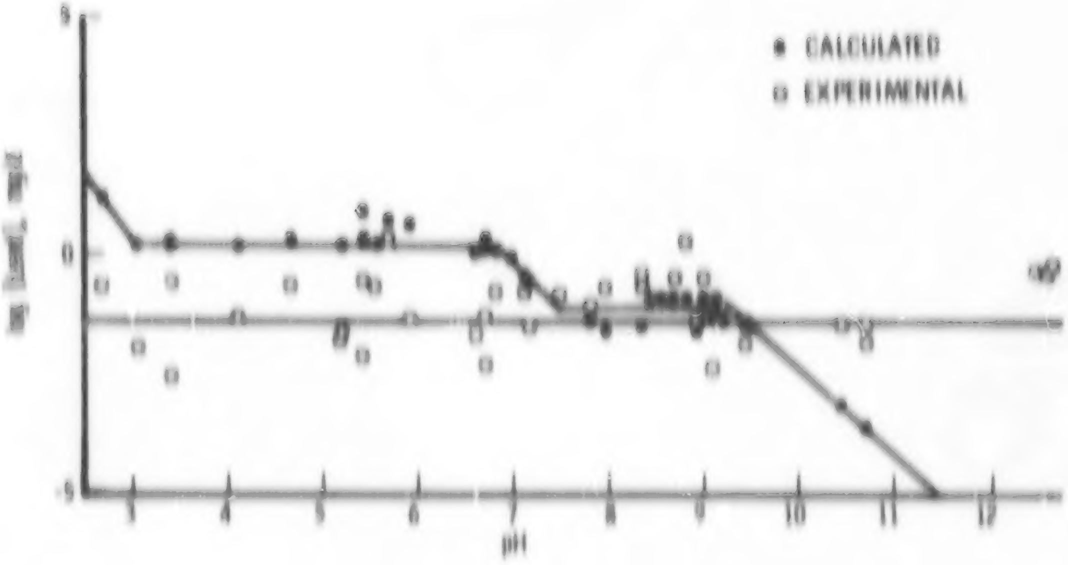

Figure F-10. Comparison of experimental and calculated concentrations of lead.

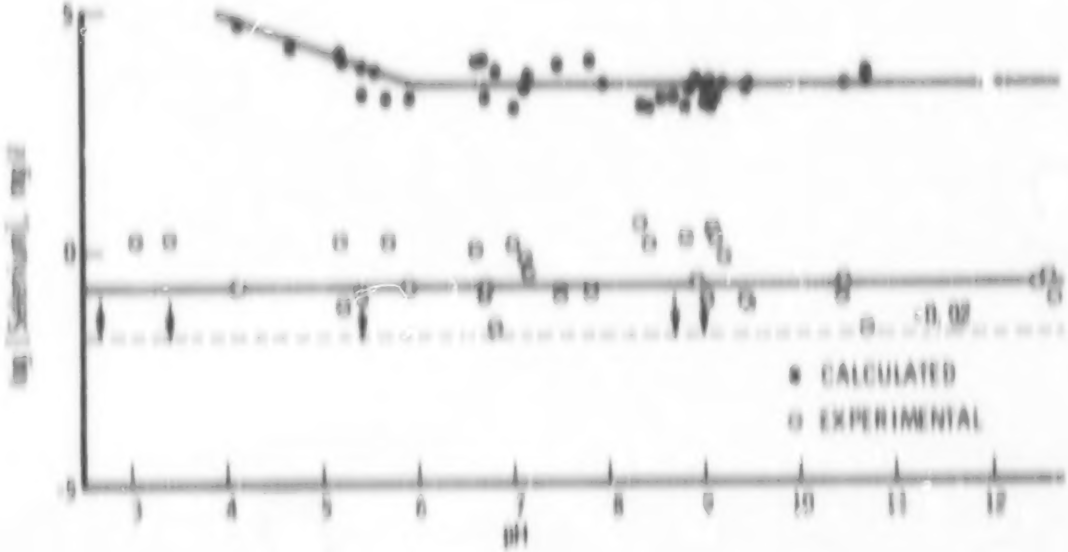

Figure F-11. Comparison of experimental and calculated concentrations of selenium.

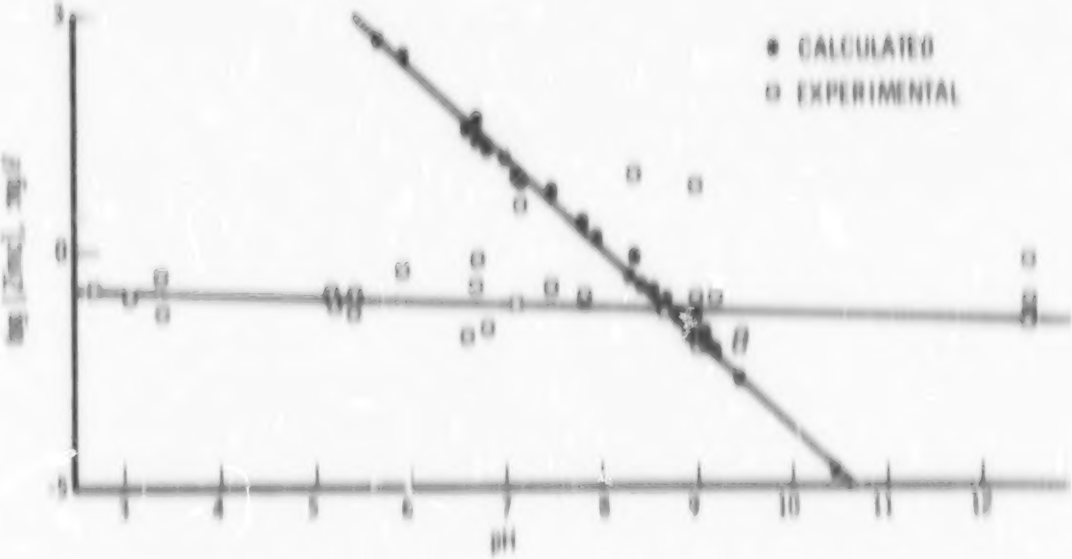

Figure F-12. Comparison of experimental and calculated concentrations of zinc.

APPENDIX G

FGC WASTE TRANSPORT COSTS

Cost data have been gathered for five methods of moving flue gas cleaning (FGC) waste products. The following methods were evaluated: (a) rail hauling, (b) trucking, (c) barging, (d) pumping, and (e) conveying. Each of these transport modes could be used separately or in combinations, depending upon the specific operational situation involved. Data have been gathered for hauling for distances up to 500 miles; however, in most instances the disposal site is expected to be within about 5 miles of the power plant. At such short travel distances, the specific characteristics of the power plant (e.g., topography and land availability) would greatly influence the hauling mode selected. Therefore, the data presented here are considered to be useful in the development of engineering estimates of the relative costs involved. All estimates were based on the output from a 1000-MW station, producing between 1700 and 4800 tons per day of sludge (50 percent solids) on a 300 day per year basis. Also, all estimates are based on one-way distances. In the case of truck rates, the quotes were made with the understanding that the trucks would return to their origin. No such specification was made on the other vehicular transport modes.

These data were used as reference material for a portion of this study which is referenced in 10.2.2 and reported in (2).

G.1 RAIL HAULING

Inquiries on hauling rates were made with railroad companies in the west, midwest, and along the eastern seaboard. The quotations received* were from existing tariff schedules, without benefit of special class rates or equipment specifically designed for the purpose of hauling sludge. Additional information was received from the Energy Research and Development Administration (ERDA)† on typical rail rates across the nation. The results, as shown in Figure G-1, indicate that rail hauling is probably not economically feasible at hauling distances of less than 50 miles at ordinary commercial rates. At 50 miles, the rates vary between 11 and 14 cents per ton-mile and decrease to between 3 and 8 cents per ton-mile at 300 miles. The estimates were made for gondola cars of at least 80 tons capacity.

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*Private communication: Union Pacific Railroad, 15 May 1975; Penn Central Transportation Company; 17 July 1975; Chessie System, 8 August 1975.

†Private communication: Murray Chais (ERDA), 18 June 1975.

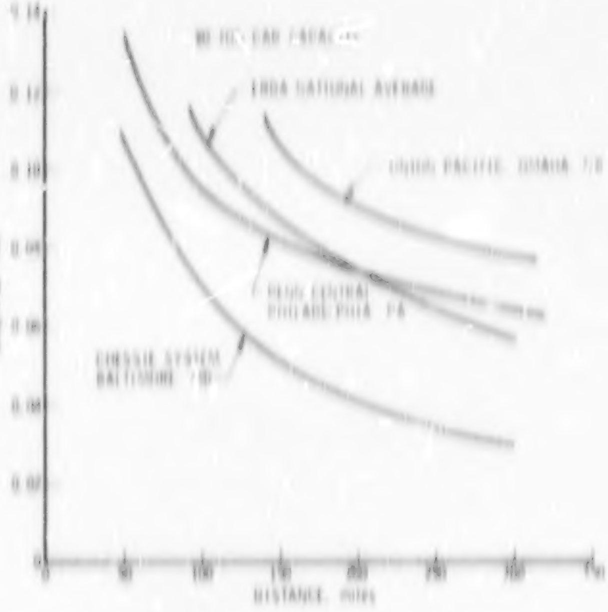

Figure G-1. Rail rates vs distance.

In view of the large quantities of sludge to be hauled, it was recommended by one of the railroad companies that the power companies should request a new class rate be established to haul this material in coal cars back to the mine (44).

G.2 TRUCK HAULING

The rates for hauling sludge in a bottom dump or trailer truck of at least 20-ton capacity vary significantly, depending on the locale involved. As shown in Figure G-2, the rate for hauling a distance of 10 miles varies between 10 and 12 cents per ton-mile in Wilmington, California, and Pittsburgh, Pennsylvania, respectively. For distances of 125 to 150 miles, these rates decrease to between 4 and 5 cents per ton-mile.[§] For longer hauling distances, on an interstate rate basis, the cost is approximately 11 cents per ton-mile at 100 miles and decreases to 9 cents per ton-mile at 350 miles.[†]

As with the railroad companies, the trucking firms contacted for rate information recommended that the power companies request a special hauling rate for the large quantities of sludge involved. One company[‡]

[§] Private communication: W. H. Hutchinson and Sons Service, 1 May 1975; R. Harrison, Harrison/Nichols, Los Angeles, 12 February 1975.

[†] Private communication: Nationwide Bulk Carrier Conference, Inc., Freight Tarriff, 11 April 1975.

[‡] Private communication: Chancellor and Ogden, Inc., Wilmington, CA.

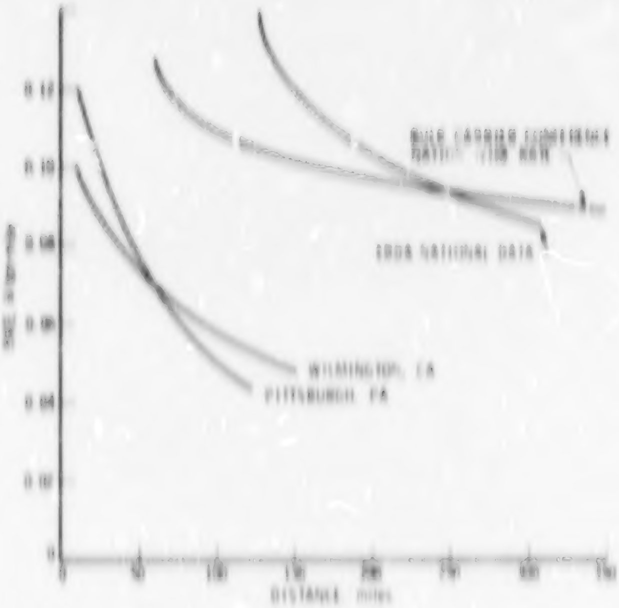

Figure G-2. Truck rates vs distance.

offered to provide new trucks specifically designed to accommodate power plant sludge disposal, including drivers, equipment, maintenance, and financing, if a contract for a period of at least five years could be negotiated.

In addition to the hauling costs, a cost must be added for loading and unloading the trucks. If the sludge is filtered, so as to minimize liquid leakage and to improve sludge handling characteristics, then the loading and discharging process would be simpler. It is estimated that a truck can be loaded with filter cake in approximately 3 to 5 min, and the discharge time would be approximately the same depending on conditions at the disposal site.

G.3 BARGE HAULING

The typical cost for hauling by a river barge with a 1400-ton capacity is about 4 to 5 mills per ton-mile along the tributaries of the Ohio and Mississippi Rivers and about 1 cent per ton-mile for the coastal-canal route from New Orleans to Brownsville, Texas.[8] The variation of barge rates with distance for the inland waterways is shown in Figure G-3 (40). These barges are 195 ft long by 35 ft wide, with a 9-ft draft, and are built with hoppers having sides of approximately 15 ft in height. The barges can handle either clarifier underflow slurry or filter cake. Barge companies have had experience handling materials of similar consistency. For example, lime slurry has been barged along the Mississippi River. In this case, the slurry was pumped onto the barge, and then at the destination a suction hose was

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[8] Private communication: John A. Welch, Federal Barge Company, Houston, Texas, 14 February 1975.

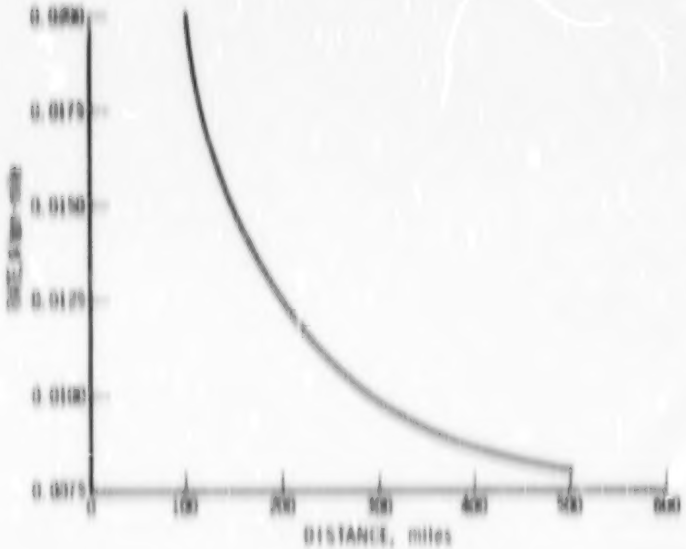

Figure G-3. Typical barge hauling costs for inland waterways.

used to remove the material. Materials of wet-sand consistency are continuously being loaded by clam shell scoops onto barges and removed in the same manner. The cost of clam shell operation is about $1/ton handled. One tug of 5 to 10,000 hp can handle up to 30 barges in a single tow. One of the barge companies indicated that materials of the type being barged are exempt from federal or state control, and, because of the large tonnage, the hauling costs could probably be negotiated for even less than the amounts noted. In fact, the barge companies would probably purchase dedicated barges for this work at $100,000 to $150,000 each. For sludge dewatered to 50 percent solids, the number of barges required for a 1000-MW scrubber is about seven every two days (3-1/2 per day). At 65 percent solids, the number of barges required is reduced to five every two days.

G.4 PUMPING

A number of long-distance pipelines are in operation which pump materials comparable to FGC waste materials (41). Many of these pipelines are between 100 and 500 miles in length, and the cost associated with their operation is a function of the tonnage transported, distance, physical characteristics of the material, terrain conditions, and the annual capital charges of the pipeline. The two cost factors which are most significant are the annual tonnages and the distance transported. For slurries, similar to FGC wastes, having a specific gravity of 1.40 and a solids concentration of 50 weight-percent, the transport cost for an annual quantity of 2 million tons is approximately 0.7 cents per ton-mile in 1971 dollars (42). For a quantity of 1 million tons per year, the cost is estimated to be 1 cent per ton-mile. These costs do not include the costs associated with preparation of the material (such as dewatering) or handling the material at its destination. However, the costs do include operating costs and capital charges. The capital charges are applied at an annual rate of 15 percent of the total capital investment.

For shorter pipeline distances, i.e., from 5 to 50 miles, the costs become site-specific. However, costs have been estimated for an average throughput of approximately 1 million tons per year (125 tons/hr), using information developed as part of the field evaluation at the TVA Shawnee plant (43). These data show that a 5-mile, 2-way pipeline system, using 500-hp pumps and a 10-in. diameter pipe on the outgoing line and 30-hp pumps and a 6-in. diameter return line, would cost approximately 6 cents per ton-mile, including capital charges and operating costs.

G.5 CONVEYING

The use of conveyor belts for transporting dewatered FGC sludge may be a cost-effective option for very short distances or when unusual or difficult transportation conditions exist. As with the other modes of transport, the cost for conveyor installations for relatively short distances will vary significantly from site to site. However, for the purpose of making an engineering estimate of the cost of conveyor operations, a quote was obtained from Bulk Systems of Detroit.* The conveyor was assumed to be 3 ft wide, with a continuous hood cover and powered by a 400-hp motor. The conveyor portion was priced at $250/ft and the overhead galleries at $560/ft. The gallery spans were assumed to be 60 ft, and the grade was assumed to have a constant 1 percent rise. For a 5-mile installation, the cost, including capital charges, is 78 cents per ton-mile in 1975 dollars. This price does not include land costs or special provisions for road crossing. Also, costs of dewatering the sludge or handling it at the disposal site are not included.

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*Private communication: J. W. Moll to L. J. Bornstein, for Bulk Systems, Detroit, Michigan, 7 April 1975.